

COURSE
OF
PRACTICAL CHEMISTRY,

AS ADOPTED AT
UNIVERSITY COLLEGE, TORONTO.

BY
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TORONTO:

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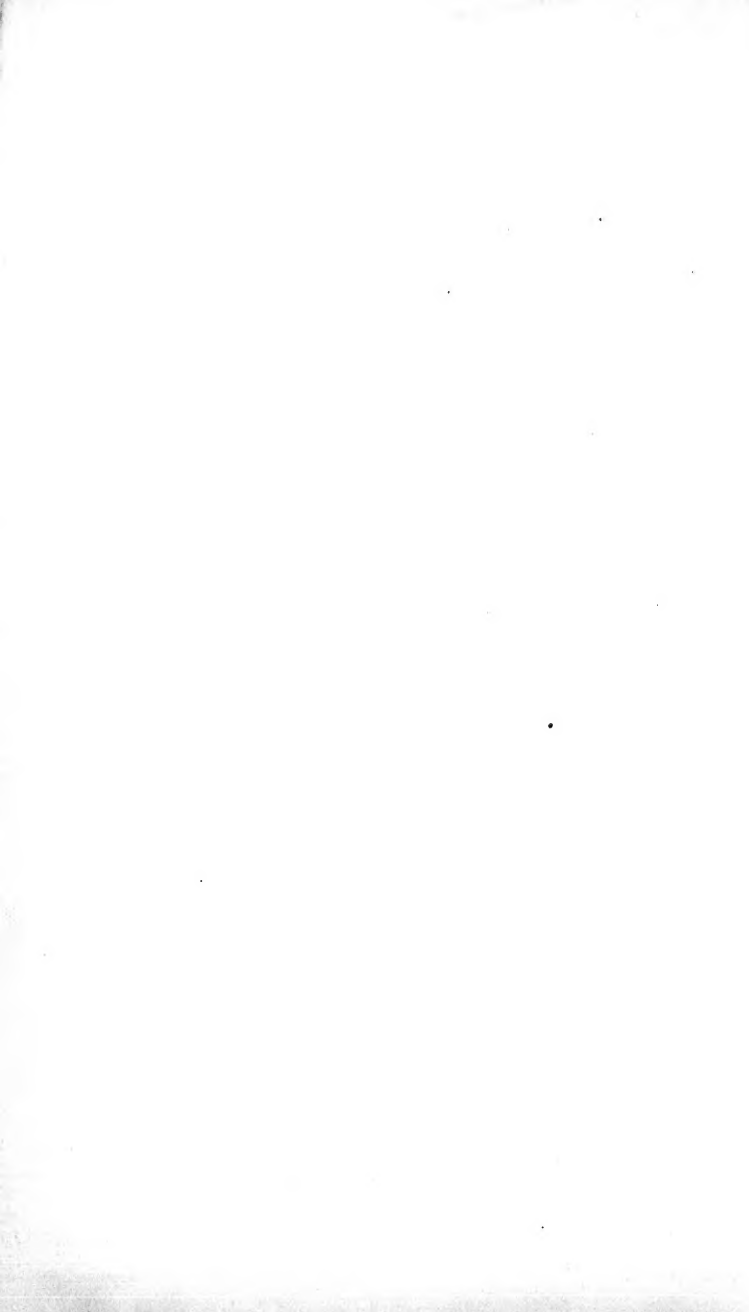
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PREFACE

The system of the book is the same as that of the first edition, but the material has been revised and brought up to date. It has been found that the book is well received by students and teachers alike, and it is hoped that this edition will be equally well received. The book is intended for use in the first year of a course in the history of the United States, and it is hoped that it will be found useful to students and teachers alike. The book is divided into two parts, the first part dealing with the history of the United States from 1776 to 1865, and the second part dealing with the history of the United States from 1865 to the present. The first part is divided into three sections, the first section dealing with the history of the United States from 1776 to 1800, the second section dealing with the history of the United States from 1800 to 1840, and the third section dealing with the history of the United States from 1840 to 1865. The second part is divided into two sections, the first section dealing with the history of the United States from 1865 to 1890, and the second section dealing with the history of the United States from 1890 to the present. The book is written in a clear and concise style, and it is hoped that it will be found useful to students and teachers alike.



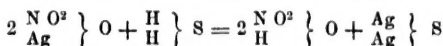
P R E F A C E .

The first edition of the small work on Practical Chemistry, used as a text book in University College, being out of print, it has been necessary to re-write the whole for the present edition, in order to introduce the new nomenclature and formulas, and also such emendations as the experience of several years has rendered advisable. Among the many formulas proposed by recent investigators, the author has confined himself to the typical and empirical, as being the simplest and most easily comprehensible. No references to authorities are given, as the work makes no claim to originality, but is simply to be used as a guide for students, especially medical, who may be taking the course of practical chemistry in our college, and as a mere introduction to the admirable works of Fresenius, Noad and Rose, which should be in the hands of every one wishing to perfect himself in analysis. Owing to the fact that philosophical apparatus is not easily obtainable in many parts of Canada, the author has been obliged to omit many methods of investigation which would otherwise have been introduced. Hence no reference is made to spectrum analysis or kindred methods of investigation.

To avoid repetition the group tests have not been repeated, except in a few instances among the special tests; and only those re-actions have been mentioned which may be considered as characteristic, and such as would be employed in the detection of the various substances.

The various re-actions described have not generally been illustrated by formulas, the construction of which will form good practice for the student, and his results may be corrected by the teacher. The student should endeavour to write out each operation by means of formulas. Thus barium nitrate and sodium sulphate give barium

sulphate and sodium nitrate. $\text{Ba. } 2 \text{ N O}^3 + \text{Na.}^2 \text{ S O}^4 = \text{Ba. S O}^4 + \text{Na.}^2 2 \text{ N O}^3$ or 2 Na. N O^3 . Silver nitrate and hydrosulphuric acid give silver sulphide and nitric acid. $2 \text{ Ag N O}^3 + \text{H}^2 \text{ S} = 2 \text{ H. N O}^3 + \text{Ag}^2 \text{ S}$. These formulas may also be written typically thus :



H. CROFT.

UNIVERSITY COLLEGE,

February, 1870.

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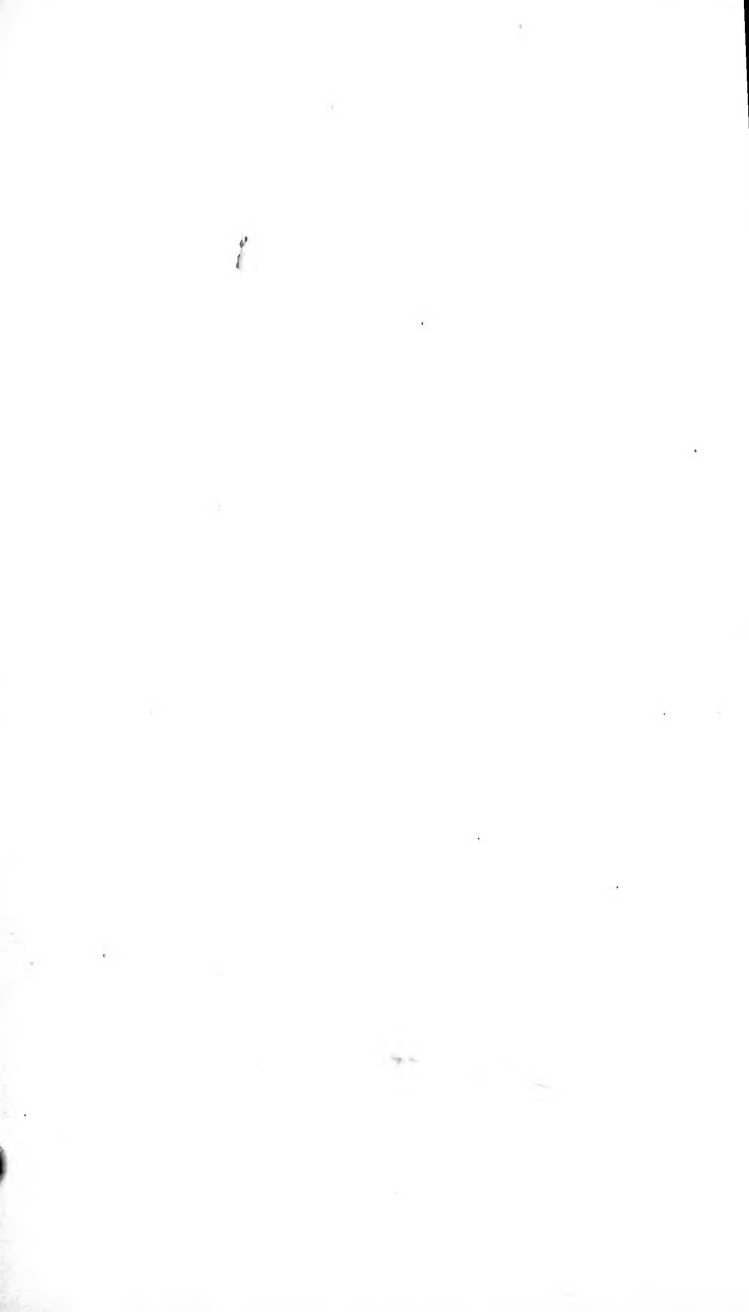
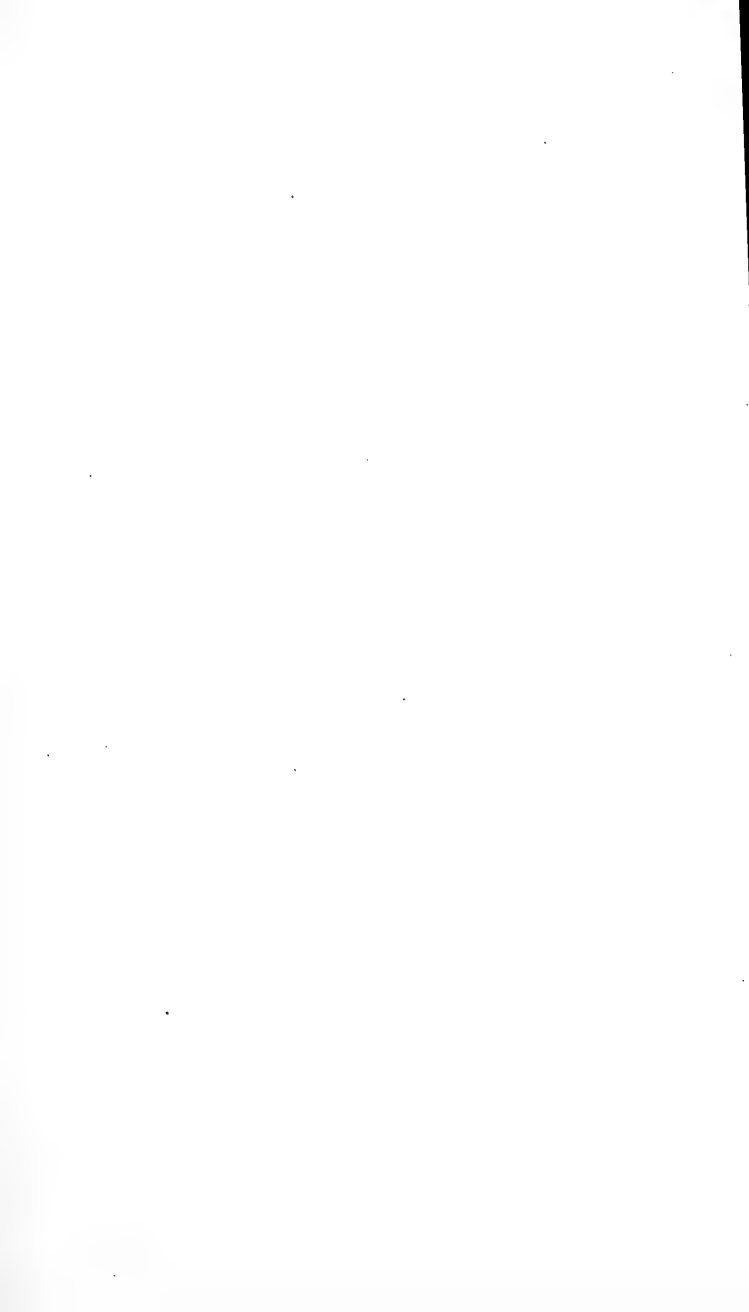


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ERRATA AND ADDENDA.



Page 17, line 33, for "presencs" read "presence"

29, 31, for "chloride" read "chlorine"

31, 36, for "used" read "fused"

34, 4, for "chlorde" read "chloride"

35, 9, for "produce" read "produces"

55, 20, for "*same*" read "*original*"

61, Under first column, read

"If ammonia has been found, some salts of the above acids will volatilise without blackening."

Under second column, read

"If ammonia has been found and nitric acid be present, the salt will decompose without deflagration."*

31, Under Ferric Salts.

Test 9. Tannic acid produces an intense black colour.

61, Under Group I.

Ferro and ferricyanides blacken somewhat on heating; they may be recognized by the tests mentioned in Table I. Group II, or by those in Table III. The precipitates formed by ferricyanides in silver nitrates is of a brownish yellow colour.

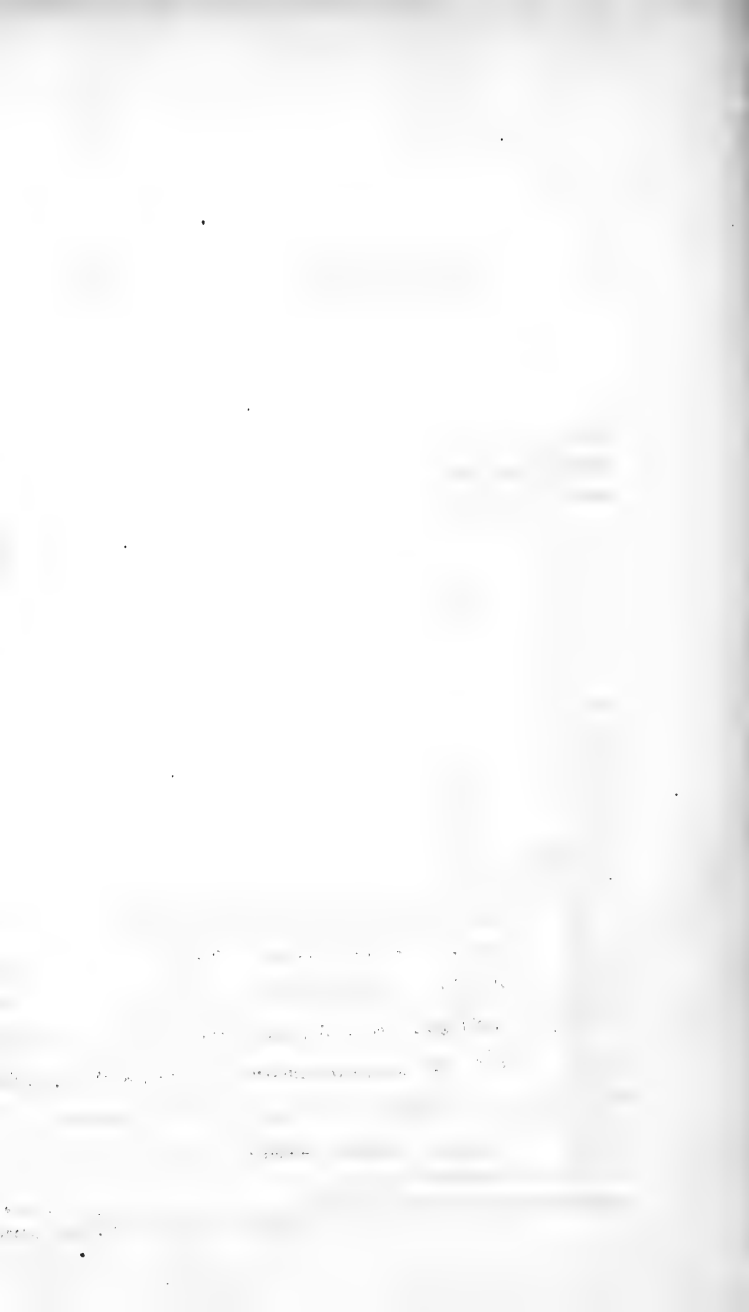
65, If a salt is given for the detection of the acid alone, without reference to the base, Table II. should be used, as chromic, arsenic, and other metallic acids, are not included in Table I. which is supposed to be employed after the detection of the base or metal. If arsenic or antimony has been found, their metals may have been present combined with bases or possibly with acids or halogens. The solution may contain arsenious chloride or potassium arsenite, &c. &c.

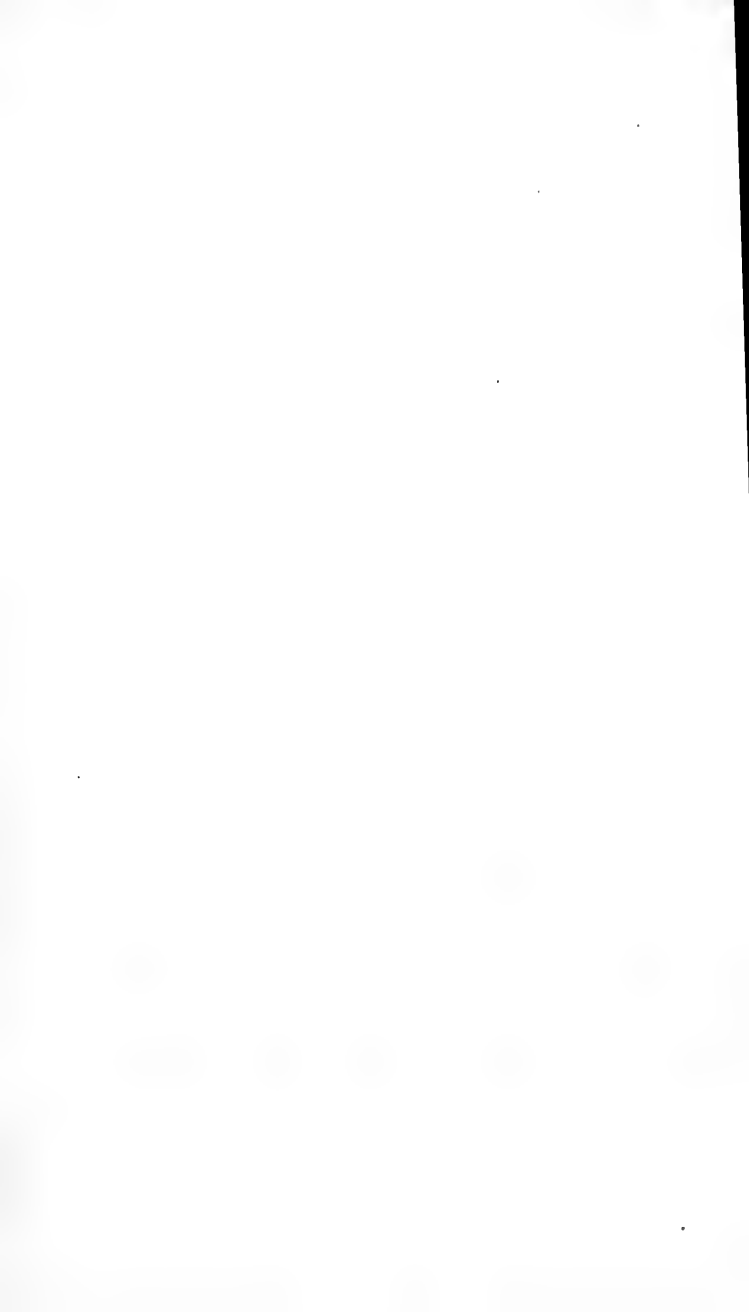
Plate. Fig. 17 is omitted, being the same as Fig. 7.

* Students should make the corrections at pages 55 and 61 before attempting to use the tables.

SYMBOLS AND ATOMIC WEIGHTS OF THE COMMONER ELEMENTS.

Oxygen	O		16	Aluminium	Al		27.5
Chlorine	Cl		35.5	Manganese	Mn		55
Bromine	Br		80	Iron	Fe		56
Iodine	I		127	Chromium	Cr		52.5
Fluorine	F		19	Nickel	Ni		58.8
Sulphur	S		32	Cobalt	Co		58.8
Phosphorus	P		31	Zinc	Zn		65
Carbon	C		12	Cadmium	Cd		112
Boron	B		11	Bismuth	Bi		208
Silicon	Si		28.5	Copper	Cu		63.5
Nitrogen	N		14	Lead	Pb		207
Hydrogen	H		1	Tin	Sn		118
Potassium	K		39	Antimony	Sb		122
Sodium	Na		23	Arsenic	As		75
Barium	Ba		137	Silver	Ag		108
Strontium	Sr		87.5	Mercury	Hg		200
Calcium	Ca		40	Gold	Au		196.7
Magnesium	Mg		24	Platinum	Pt		197.4





PRACTICAL CHEMISTRY.

RE-AGENTS.

In the following list all the principal re-agents that are required are mentioned by their old and new names, and by their old and new formulas. The typical formulas have also been added. The water of crystallisation has been omitted.

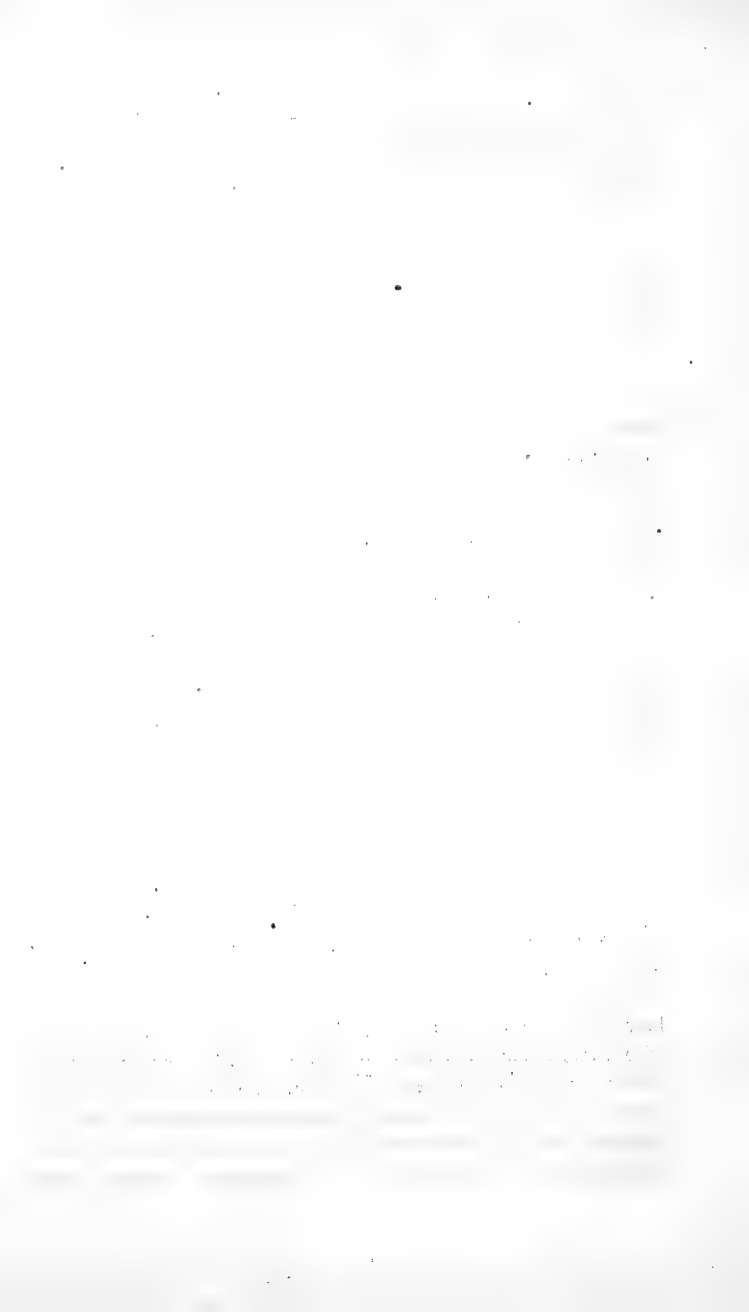
OLD.		EMPIRICAL.	TYPICAL.
Sulphuric Acid..... H O. S O^3	Sulphuric Acid	$\text{H}^2. \text{S O}^4$	$\text{S O}^2 \left. \begin{array}{l} \text{H}^2 \end{array} \right\} \text{O}^2$
Nitric Acid	Nitric Acid	H. N O^3	$\text{N O}^2 \left. \begin{array}{l} \text{H} \end{array} \right\} \text{O}$
Hydrochloric Acid..... H Cl	Hydrochloric Acid.....	H Cl	$\text{Cl} \left. \begin{array}{l} \text{H} \end{array} \right\}$
Hydrosulphuric Acid H S	Hydrosulphuric Acid.....	$\text{H}^2. \text{S}$	$\text{H} \left. \begin{array}{l} \text{H} \end{array} \right\} \text{S}$
Water	Water	$\text{H}^2 \text{O}$	$\text{H} \left. \begin{array}{l} \text{H} \end{array} \right\} \text{O}$
Oxalic Acid	Oxalic Acid..	$\text{H}^2. \text{C}^2 \text{O}^4$	$\text{C}^2 \text{O}^2 \left. \begin{array}{l} \text{H}^2 \end{array} \right\} \text{O}^2$
Acetic Acid $\text{H O. C}^4 \text{H}^3 \text{O}^3$	Acetic Acid.....	$\text{H. C}^3 \text{H}^3 \text{O}^2$	$\text{C}^3 \text{H}^3 \text{O} \left. \begin{array}{l} \text{H} \end{array} \right\} \text{O}$
Tartaric Acid... $\text{H O. C}^4 \text{H}^4 \text{O}^5$	Tartaric Acid	$\text{H}^2. \text{C}^4 \text{H}^4 \text{O}^6$	$\text{C}^4 \text{H}^4 \text{O}^4 \left. \begin{array}{l} \text{H}^2 \end{array} \right\} \text{O}^2$
Ammonia	This when in solution may be considered as Ammonium Hydrate...	$\text{N H}^4. \text{H O}$	$\text{N H}^4 \left. \begin{array}{l} \text{H} \end{array} \right\} \text{O}$
Potassa	Potassium Hydrate.....	K. H O	$\text{K} \left. \begin{array}{l} \text{H} \end{array} \right\} \text{O}$
Soda	Sodium Hydrate	Na. H O	$\text{Na} \left. \begin{array}{l} \text{H} \end{array} \right\} \text{O}$
Slaked Lime	Calcium Hydrate.....	$\text{Ca. H}^2 \text{O}^3$	$\text{Ca} \left. \begin{array}{l} \text{H}^2 \end{array} \right\} \text{O}^3$
Carbonate of Soda Na O. C O^2	Sodium Carbonate...	$\text{Na}^2. \text{C O}^3$	$\text{C O} \left. \begin{array}{l} \text{Na}^2 \end{array} \right\} \text{O}^3$
* Carb. of Ammonia $\text{NH}^4 \text{O. CO}^2$	Ammonium Carb..	$(\text{N H}^4)^2. \text{C O}^3$	$\text{C O} \left. \begin{array}{l} (\text{N H}^4)^2 \end{array} \right\} \text{O}^3$
Chloride of Barium..... Ba Cl	Barium Chloride.....	Ba Cl^2	$\text{Ba} \left. \begin{array}{l} \text{Cl}^2 \end{array} \right\}$

* The salt usually employed is really a sesquicarbonate mixed generally with some bicarbonate, hence ammonia is added to the solution.

Chloride of Calcium Ca Cl	Calcium Chloride Ca Cl ²	Ca } Cl ² }
Chlor. of Ammonium..N H ⁴ Cl	Ammonium Chloride ...N H ⁴ Cl	N H ⁴ } Cl }
Perchloride of Iron ...Fe ² Cl ³	Ferric Chloride Fe ³ Cl ⁶	Fe ³ } Cl ⁶ }
Bichloride of Platinum Pt Cl ²	Platinic Chloride or Platinum Tetra Chloride Pt Cl ⁴	Pt } Cl ⁴ }
Protochloride of Tin ...Sn Cl	Stannous Chloride Sn Cl ²	Sn } Cl ² }
Chloride of Magnesium Mg Cl	Magnesium Chloride.....Mg Cl ²	Mg } Cl ² }
Sulphate of Copper Cu O. S O ³	Cupric Sulphate Cu. S O ⁴	S O ³ } O ² Cu }
Sulph. of Magnesia Mg O. S O ³	Magnesium Sulphate..Mg. S O ⁴	S O ³ } O ² Mg }
Carbonate of Lime Ca O. C O ³	Calcium Carbonate Ca. C O ³	C O } O ² Ca }
Ferrocyanide of Potm. K ¹ Cfy	Potm. Ferrocyanide.....K ⁴ Cfy	Cfy } K ⁴ }
Ferricyanide of Potm. K ³ Cfdy	Potm. Ferricyanide K ³ Cfy	Cfy } K ³ }
Sulphocyanide Potm K S. Cy S	Potm. Sulphocyanate...K. Cy S	Cy } S K }
Phosphate of Soda Na ³ O ² . H O. P O ⁵ }	Sodium Phosphate..Na ² H. P O ⁴	P O } O ² Na ³ H }
Oxalate of Ammonia NH ⁴ O. C ² O ³ }	Ammonium Oxalate(NH ⁴) ² . C ² O ⁴	C ² O ² } O ² (N H ⁴) ² }
Acetate of Soda Na O. C ⁴ H ³ O ³	Sodium Acetate ...Na. C ² H ³ O ²	C ² H ³ O } O Na }

NOTES ON TESTING.

In the application of re-agents some judgment is required as to the quantity to be employed and the manner of using them. For instance, solutions of hydrosulphuric acid, ammonium chloride sodium phosphate, sodium hyposulphite, calcium sulphate, and some others, should be used in considerable quantities, while a few drops of ammonium sulphide, potassium ferrocyanide, &c. &c., will be sufficient to produce the result required. No more of a re-agent should be used than is sufficient to produce the desired re-action. In many cases violent agitation assists the formation of a precipitate, as in testing for barium with sodium hyposulphite, for magnesium by ammonia and sodium phosphate, or potassa by tartaric acid. The test tube should be held between the first and second finger, and closed by the thumb.





When it is stated that a precipitate is soluble in excess, it will be well in many cases to throw away the greater part of the precipitate and use only a small portion, as otherwise a very large amount of the solvent may be required (lead chromate and oxide, calcium tartrate, &c. &c.). In trying the action of acids on precipitated sulphides, it is necessary to allow the precipitate to settle, to pour off the liquid, and to repeat this operation a few times with the addition of water. The sulphide may also be collected on a filter, washed, the acid poured on, and the filter broken by a rod, so as to allow the mixture to run into a test tube. If this is not attended to the acid may be too dilute to show the re-action.

In boiling any substance with acids it will be well for the operator always to turn the mouth of the test tube away from him, and in testing salts care should be taken that the substance is thoroughly dissolved and a uniform mixture obtained by shaking,

In examining the action of acids upon precipitated sulphides the operator should avoid an excess of ammonium sulphide (if this reagent has been used), as in most cases a white opalescence will be produced from separation of sulphur. This may easily lead to error where white precipitates have been formed, as with salts of zinc and alumina, and possibly with salts of manganese. A quantity of ammonium sulphide should be added, insufficient to precipitate the whole of the metal; or, if excess has been employed, the precipitate should be collected on a filter and well washed out before applying the acid.

APPARATUS REQUIRED.

Two dozen test tubes, about six inches long and of such a diameter that they can be perfectly closed by the thumb. When held thus closed between the first and second fingers, solutions can be violently shaken by a rapid oblique motion. When the liquid is of a corrosive character it may be shaken by holding the tube between the thumb and first finger, with the assistance of the second and third. As these tubes are not a regular article of trade with us, they should be reserved as far as possible for experiments in which violent agitation is required or the application of heat necessary.

Most of the ordinary precipitations can be effected in small glasses, readily manufactured from 1 oz. or 2 oz. phials by cutting off the neck and shoulders by a filed scratch and the application of a hot wire.

A blow-pipe and lamp. The common lamp so much used with us for burning fluid will answer admirably, especially if the wick be made somewhat larger than usual; or a small coal oil lamp with flat wick may be used, the burning fluid employed being made by shaking together one part oil of turpentine with eight parts alcohol.

Platinum wire and stiff foil.

A few small flasks, porcelain crucibles, funnels and dishes.

A spirit lamp; a small coal oil lamp will answer, if filled with alcohol.

A water bath; a small tin saucepan will answer, if provided with tin covers with holes of different diameters.

Some thin glass tubing for making reduction tubes; it may be cut into lengths of about eight inches, and drawn out in the centre by heating in the blowpipe flame. The glass should be very thin. Some glass rods for stirring; tubes closed at each end will answer.

Some plates or strips of glass, watch glasses, wire triangles, filtering paper, files both round and triangular, test tube cleaner made by tying some sponge on to a piece of wood, vulcanised rubber tubing, test tube stand, retort stand or iron tripod, will also be required.

The bottles for the solutions of the various re-agents may be of any moderate size, and those for the acids must have glass stoppers. Corks may be used for most of the other solutions.

A spirting bottle or flask will be found useful for washing out precipitates, and several 10 or 12 oz. bottles will be required for evolving sulphuretted hydrogen and other gases.

RE-AGENTS NOT IN THE FORM OF SOLUTION.

The principal bodies of this nature referred to in the following pages are borax, nitre, microcosmic salt, and some hydrates.

Borax must be heated till it swells up and loses all its water of crystallisation, it need not be fused, a small loop having been made

in a piece of platinum wire and heated red hot, some of the powdered borax will adhere to it on contact, this can then be fused in the outer flame of the blow-pipe and the operation repeated until a sufficiently large and clear bead has been obtained.

Nitre may be purified by two or three crystallisations.

Microcosmic salt (sodio ammonium phosphate) may be prepared by dissolving together 6 parts of sodium phosphate and 1 part of ammonium chloride in 2 parts of water and allowing to crystallise. The salt should be purified by re-crystallisation; when heated on wire or charcoal it froths, loses ammonia and leaves a clear bead of sodium metaphosphate which possesses the property of dissolving many metallic oxides with their characteristic colours.

HYDRATED FERRIC OXIDE.

FERRIC HYDRATE.

Is not used as a re-agent, but may be required as an antidote to arsenious acid. It may be prepared by dissolving iron nails in dilute sulphuric acid, or green vitriol (ferrous sulphate) in water, boiling and adding nitric acid until the black colour at first produced disappears and the solution becomes yellow. The acid must be added somewhat carefully as effervescence takes place towards the end of the operation. The solution is mixed with ammonia in moderate excess after being cooled, the brownish red precipitate is collected on a filter and washed with water until the washings exhibit no trace of hydrochloric or sulphuric acid. It should be kept under water and should be prepared at least once a year, as the hydrate by keeping becomes more dense, from change of composition, and loses to a great extent its power of separating arsenious acid from its solutions. It also becomes much more difficultly soluble in hydrochloric acid.

HYDRATED MAGNESIUM OXIDE.

MAGNESIUM HYDRATE.

Is also recommended as an antidote for arsenious acid either by itself or in conjunction with ferric oxide. It may be obtained by precipitating magnesium sulphate with slight excess of potassium hydrate and treating as above described.

When an arsenite has been used, ferric or magnesium acetate should be added to the hydrate.

HYDRATED BISMUTHIC OXIDE.**BISMUTHIC HYDRATE.**

The officinal subnitrate of bismuth is dissolved in water with the addition of as little nitric acid as possible, ammonia is then added in excess and the whole digested for some time, filtered, washed and dried by exposure to the air. This substance is sometimes useful for decomposing an alkaline solution of arsenious sulphide. It may, however, be dispensed with, as the sulphide may be converted into an oxide by repeated boiling with nitric acid.

SODIUM CARBONATE.

Is obtained tolerably pure by heating the officinal carbonate to dull redness for some time.

POTASSIUM CYANIDE.

Can be purchased sufficiently pure in photographic establishments.

LEAD BINOXIDE.

Obtained by treating red lead with nitric acid until of a brown colour and washing out well with distilled water. Red lead may generally be substituted.

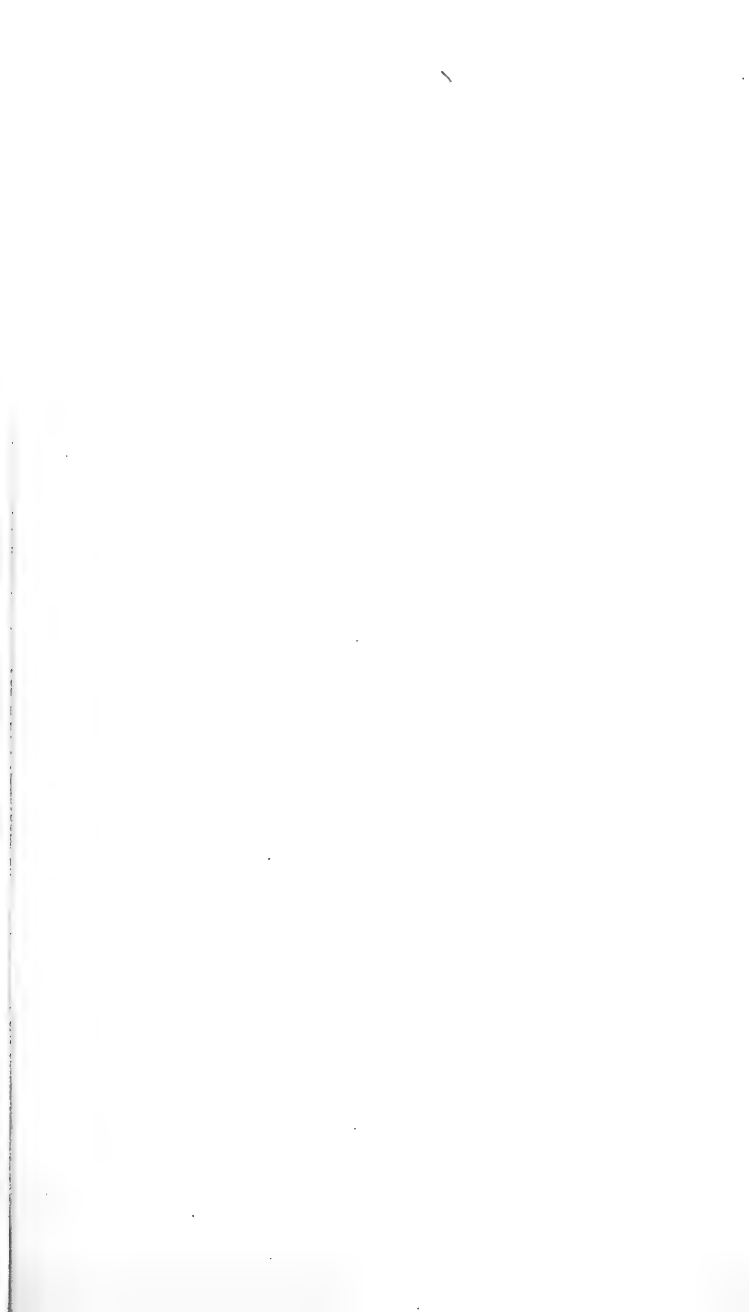
POTASSIUM BICHROMATE.

The commercial salt is sufficiently pure if re-crystallised.

RE-AGENTS IN A LIQUID FORM.**SULPHURIC ACID.**

This acid is employed either in its concentrated form, or diluted with five or six parts of water. It often contains arsenic, which may be detected by the formation of a yellow precipitate on passing hydrosulphuric acid gas through the diluted acid, or better by the test mentioned at page 41. Lead sulphate is frequently present, and forms the white sediment often observed on diluting the acid; the lead can be detected by pouring carefully moderately strong hydrochloric acid on to the concentrated acid, so as not to mix with it. A white film at the point of junction (lead chloride) indicates





lead. Nitric acid is sometimes present, and may be detected by heating the concentrated acid with a few drops of solution of indigo (sulphindigotic acid); if nitric acid be present, the blue colour will be changed to yellow or brown. It may also be detected by mixing the concentrated acid with an equal bulk of water, cooling, and throwing in a crystal of ferrous sulphate, or pouring a solution of that salt on to the acid. A brown colouration round the crystal, or between the liquids, indicates nitric acid; the solution should not be shaken. The acid should always be added *to the water* with which it is to be diluted under constant agitation, and the student will do well to add the above mentioned substances to an acid which he has found to be pure, and to apply the tests for their detection.

NITRIC ACID.

Often contains hydrochloric acid, which may be detected by the formation of a white curdy precipitate on the addition of silver nitrate after dilution; when only a trace is present, nothing more than an opalescence will be observed.

Sulphuric acid may be detected by adding barium chloride or nitrate to the *strongly* diluted acid; a white precipitate will be produced. It is necessary to dilute largely, as otherwise a crystalline precipitate of barium nitrate will be formed, which might be mistaken for sulphate, but is readily dissolved on the addition of excess of water.

HYDROCHLORIC ACID.

Sulphuric acid may be detected by barium chloride or nitrate, added to the strongly diluted acid; the chloride is insoluble in strong hydrochloric acid, and hence it must be diluted before the test is applied.

Sulphurous acid may be detected by adding a piece of metallic zinc to the somewhat diluted acid, and placing a piece of paper smeared with lead acetate or carbonate in the tube; if sulphurous acid be present the lead paper will be turned brown or black by the hydrosulphuric acid evolved.

It may also be detected by mixing the acid with a little nitric acid, boiling, diluting with water, and adding a salt of barium; a white precipitate which was not produced previously to this treatment will indicate the presence of sulphurous acid.

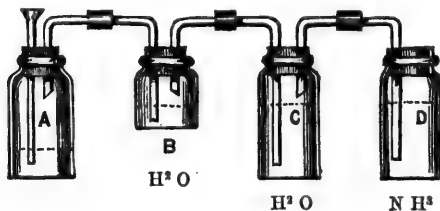
Free chlorine may be detected by its decolourising action on sulphindigotic acid when heated.

Iron may be detected by fully neutralising the acid with ammonia and adding ammonium sulphide. A black precipitate will be produced, or if only a very small quantity be present, a greenish colouration.

The iron can be further detected by acidulating the ammoniacal solution with acetic acid and adding potassium ferrocyanide, when a blue colour will be produced.

HYDROSULPHURIC ACID.

This re-agent is employed in the form of gas or as solution, which must be prepared as required. It is made by the action of dilute sulphuric acid on ferrous sulphide contained in a bottle (A. plate I.), which latter compound is most readily prepared by projecting portions of a mixture of 31 parts iron filings or turnings and 20 parts ground sulphur into a red hot earthen crucible, waiting after each addition until the vivid incandescence has ceased. The solution decomposes rapidly and is of no use unless it smells strongly of the gas, and must therefore be frequently prepared; it is better to use the old liquid, from which the gas has escaped instead of fresh water. As a large portion of the gas passes through the water (C) unabsorbed, it is well to attach a bottle containing ammonia (D), by which means ammonium sulphide may be obtained at the same time. Some particles of iron are apt to pass over, which can be detected by the liquid giving a black precipitate or green colour on the addition of ammonia, hence the use of the washing bottle (B). The tubes are connected by vulcanised caoutchouc tubing; the long funnel may be replaced by a wide tube and small funnel.







TARTARIC ACID.

The commercial acid is generally pure; it may be dissolved in 8 parts of water, but the solution cannot be kept for any length of time, as it decomposes. The same applies to the hydric sodium tartrate (bitartrate of soda).

OXALIC ACID.

The commercial acid is usually sufficiently pure, and may be dissolved in eight or ten parts of water; the solution undergoes no change by keeping.

ACETIC ACID.

The commercial *acidum aceticum fortissimum* is sufficiently strong and pure for most purposes. It sometimes contains traces of sulphuric acid detected by barium nitrate, and occasionally traces of hydrochloric acid detected by silver nitrate. In applying this test the solutions should be dilute, as silver acetate is difficultly soluble.

IODIC ACID.

The acid is required in testing for sulphurous acid and for morphine, and the potassium salt in testing for arsenic. The latter may be easily prepared by adding iodine to a boiling solution of potassium hydrate as long as it is dissolved without colouration; on cooling potassium iodate separates out, which may be collected on a filter and washed. To prepare the acid, the following process is the best: Digest at a gentle heat equal parts of iodine and potassium chlorate with 8 or 10 parts of water and a few drops of nitric acid until the iodine is dissolved. Add barium chloride as long as any precipitate is formed, and digest the washed and dried barium iodate with one-fifth of its weight of strong sulphuric acid. Filter and evaporate to a syrup. On standing, especially over sulphuric acid, the iodic acid will crystallize out of the solution.

AMMONIA.

The solution of the gas in water, *liquor ammoniæ*, is generally quite pure, the presence of carbonate may be detected by calcium chloride and of lime by oxalic acid. For precipitating cobalt, nickel and silver oxides the solution should be largely diluted. In

explaining the action of ammonia it may be supposed to exist in solution as the hypothetical ammonium hydrate $N H^4. H O - \left. \begin{smallmatrix} N H^4 \\ H \end{smallmatrix} \right\} O$

AMMONIUM CARBONATE.

The commercial salt is usually sesquicarbonate and may be dissolved with very gentle heat in four parts of water, and one part of ammonia added. It is generally very pure. Sulphuric and hydrochloric acid may be detected by barium and silver nitrate after neutralisation with nitric acid, as otherwise barium or silver carbonates would be precipitated.

POTASSIUM HYDRATE (POTASSA).

This is often very impure, containing large quantities of carbonate and chloride and small quantities of sulphate, silicate, aluminate, and sometimes lead oxide.

The presence of carbonate may be proved by the effervescence caused by the addition of nitric acid.

The chloride by a white precipitate produced by silver nitrate after supersaturation with nitric acid.

The silicate, by evaporating the supersaturated solution to dryness and washing with water; if silicate be present an insoluble residue of silicic acid will remain undissolved.

The aluminate by adding to the original solution ammonium chloride; a white precipitate indicates alumina.

When pure potassium hydrate is required, it is best prepared from the crystallised bicarbonate or from incinerated hydric tartrate (bitartrate) repeatedly crystallised. Sodium hydrate is generally much purer.

POTASSIUM CARBONATE.

This is usually so impure as to be unavailable for most analytical experiments; the bicarbonate $K H. C O^3$ or $\left. \begin{smallmatrix} C O \\ K H \end{smallmatrix} \right\} O^2$ is generally pure and may be converted into carbonate $K^2. C O^3 - \left. \begin{smallmatrix} C O \\ K^2 \end{smallmatrix} \right\} O^2$ by heating.

SODIUM HYDRATE.

This is now an article of commerce in a very pure form, and can be prepared in solution from the crystallised sodium carbonate by means of lime. It is usually free from most of the impurities which



accompany potassium hydrate, and may therefore be substituted for that re-agent with advantage.

SODIUM CARBONATE.

The carbonate and bicarbonate usually contain traces of sulphate and chloride which may be detected by adding barium or silver nitrate after supersaturation with nitric acid. If required perfectly pure, as for toxicological purposes, the bicarbonate (carbonate of the druggists) should be washed with water until the washings contain no trace of sulphate or chloride, detected as above. The residual salt may be dried and heated nearly to fusion to obtain the carbonate.

For decomposing siliceous minerals a mixture of sodium and potassium carbonate is desirable, as it fuses at a lower temperature than the individual salts. It may be obtained in a pure state by incinerating Rochelle salt, the double potassium-sodium tartrate, until all the carbon is burnt away.

BARIUM HYDRATE.

This re-agent is not often required in qualitative analysis, unless for separating magnesia from the alkalies. It may be conveniently prepared by adding a strong solution of potassium hydrate to a saturated solution of barium chloride, washing the precipitate until the filtrate contains no chloride and dissolving the residue in water and filtering. It can also be obtained in quantity by heating barium sulphate with charcoal, digesting the reduced mass with water and boiling with cupric oxide until the solution gives no black precipitate with lead acetate. The filtered solution is usually pure, sometimes of a blue colour from the presence of a trace of copper, which can be removed by adding a few drops of ammonium sulphide, boiling and filtering. The solution absorbs carbonic acid rapidly from the air, and must be kept in closely corked vessels.

It may also be prepared by heating the carbonate with charcoal and extracting the mass with boiling water.

CALCIUM HYDRATE.

The solution is useful in the detection of carbonic, tartaric and citric acids; it is prepared by pouring water over slaked lime, allowing the mixture to stand for some hours, frequently stirring. The first washings should be rejected, as they often contain potas-

sium hydrate. The solution is filtered with as little exposure to air as possible and preserved in well corked bottles.

CALCIUM CARBONATE.

The perfectly pure salt is sometimes required, and may be prepared by dissolving chalk or marble in dilute hydrochloric acid, adding ammonia until the liquid is alkaline, filtering, and precipitating the filtrate with ammonium carbonate. The snowy white precipitate must be well washed and dried.

CALCIUM CHLORIDE.

The solution is obtained by digesting dilute hydrochloric acid with the above carbonate until perfectly neutral, and filtering. The solution should not be coloured by ammonium sulphide, and should not evolve ammonia when boiled with potassium hydrate.

BARIUM CHLORIDE AND NITRATE.

These two salts can be purchased in most drug stores, and may be purified by repeated crystallization. They sometimes contain traces of lead and iron, which may be removed by hydrosulphuric acid or ammonium sulphide. One part of the salt may be dissolved in fifteen parts of water. The nitrate is often preferable to the chloride, and it must be remembered that both, though tolerably soluble in water, are difficultly soluble in both nitric and hydrochloric acids.

POTASSIUM CYANIDE.

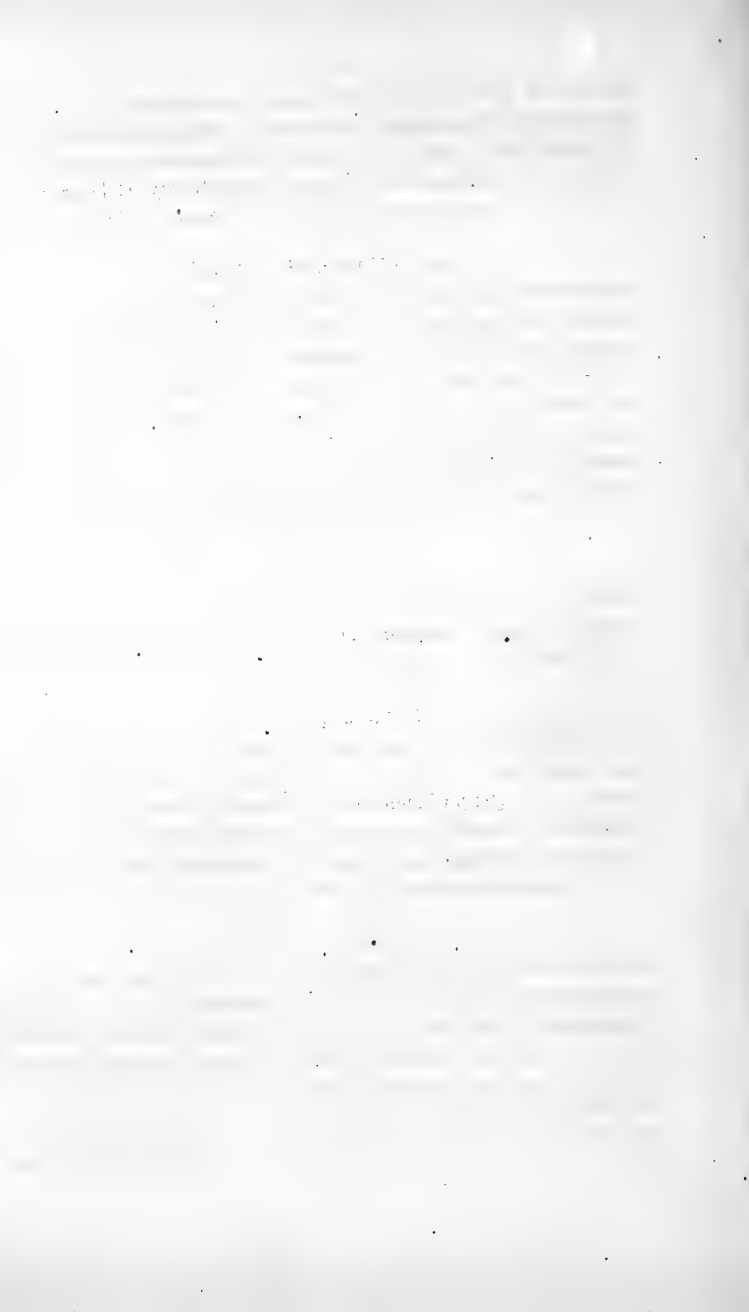
May be obtained at the photographic establishments and at most drug stores. One part of dry salt must be dissolved in four parts of water, but the solution cannot be kept for any length of time without decomposing.

POTASSIUM FERROCYANIDE.

May be purchased sufficiently pure, and dissolved in twelve parts of water. The solution remains unchanged.

POTASSIUM FERRICYANIDE.

May be purchased in some stores, or may be prepared by passing chlorine into the above named solution of ferrocyanide until a colour of it no longer gives a blue precipitate with ferric chloride, but a brown colour. The solution should be contained in a large bottle.





which can be closed and shaken from time to time to aid the absorption of the chlorine. No more of this gas should be employed than just sufficient to produce the above change. The solution is concentrated to crystallisation; the salt must be dissolved in water when required, as the solution is apt to decompose.

POTASSIUM SULPHOCYANATE.

Can be purchased in some drug stores, or may be made by fusing at a gentle heat, in an iron crucible or pan furnished with a cover, 46 parts dry ferrocyanide, 17 potassium carbonate, and 32 sulphur, until the whole mass fuses tranquilly. The heat should then be raised to faint redness. Boiling alcohol of 80 per cent. extracts the sulphocyanate from the cold mass, and yields crystals on evaporation.* Ammonium sulphocyanate may be made in a few minutes by boiling ammonium sulphide with hydrocyanic acid until the solution is colourless and inodorous.

MAGNESIUM SULPHATE.

One part of the officinal salt may be dissolved in ten parts of water. The chloride obtained by fully saturating dilute hydrochloric acid with magnesium oxide or carbonate may be used instead.

FERROUS SULPHATE.

The salt may be prepared in a very pure state by dissolving the residue left in the bottles employed for making hydrosulphuric acid. The solution is boiled, filtered and evaporated rapidly to crystallisation. The crystals should be dried rapidly and kept in well corked bottles. It can be obtained in a still purer and more permanent form by precipitating the above solution by excess of alcohol.

FERRIC CHLORIDE.

The solution is obtained by dissolving iron nails or wire in dilute hydrochloric acid, continuing the heat until no more hydrogen is evolved even with excess of the metal. Chlorine is then passed into the solution as described under potassium ferricyanide until a

* Although an iron crucible is universally recommended, a common earthenware one will answer equally well, indeed is rather better, as the iron pot is often melted if too much heat be employed.

drop of it gives no blue colour with that salt. The fluid may be diluted to twenty times the weight of the iron dissolved. The official tincture of iron often contains ferrous chloride, the presence of which may be detected by potassium ferricyanide. The solution must be perfectly free from excess of acid, the least drop of ammonia should produce a permanent precipitate.

SILVER NITRATE.

The commercial salt, especially that used by photographers, is sufficiently pure and may be dissolved in twenty parts of water.

LEAD ACETATE.

The commercial salt may be dissolved in ten parts of water.

MERCURIC CHLORIDE.

Corrosive sublimate may be dissolved in from sixteen to twenty parts of water.

CUPRIC SULPHATE.

The commercial salt may be re-crystallised several times and dissolved in ten parts of water. A very pure salt may be obtained by dissolving the residue left in the preparation of sulphurous acid from sulphuric acid and metallic copper, filtering and evaporating to crystallisation.

STANNOUS CHLORIDE.

Concentrated hydrochloric acid is boiled with excess of tin filings or tin powder (obtained by rubbing melted tin in a mortar till it becomes solid) until no more hydrogen is evolved. The solution should be filtered and kept in bottles with a small piece of metallic tin. It is rather apt to decompose by exposure and oxidation and consequently becomes useless. A white precipitate shows that the change is taking place.

PLATINIC CHLORIDE.

This salt, also called platinum tetrachloride, is obtained by dissolving the metal in nitro-hydrochloric acid and evaporating in a water bath until acid vapours are no longer evolved. The residue may be dissolved in ten parts of water.

ATTESTATION

Notary Public for the State of New York

In and for the County of New York

I, the undersigned

Notary Public for the State of New York

do hereby certify that

the foregoing is a true and correct copy

of the original of the same

as the same appears from the records

of the said Notary Public

Witness my hand and seal

this 1st day of

1900



AURIC CHLORIDE.

The salt formerly called terchloride of gold may be obtained from the photographers and dissolved in thirty parts of water. It is not absolutely required as a re-agent.

SODIUM PHOSPHATE.

The officinal salt contains small traces of sulphate which may be detected by the imperfect solubility in hydrochloric acid of the precipitate produced by barium salts. The salt may be prepared by digesting burnt bones with two-thirds of their weight of sulphuric acid for twenty-four hours, diluting, filtering, washing out, adding sodium carbonate as long as effervescence is produced, filtering and evaporating to crystallisation. The salt thus obtained always contains some sulphate unless repeatedly crystallised.

It may be dissolved in twelve parts of water.

AMMONIUM OXALATE.

Add ammonia to a hot solution of oxalic acid in two parts of water until the liquid is alkaline and allow to cool. The mother liquor drained off from the crystals will yield more of the salt on evaporation. Dissolve in twenty-four parts of water.

SODIUM ACETATE.

Neutralise acetic acid with sodium carbonate, filter and evaporate to crystallisation. Dissolve the salt in ten parts of water.

SODIUM HYPOSULPHITE.

The salt employed by photographers may be dissolved in six or eight parts of water; and the solution is preferable as a test to the fluosilicic acid, which is troublesome to prepare.

SPECIAL TESTS.

It will be advisable for the student, in the first place, to learn the special reactions by which the various metals and their oxides are distinguished, and in the following pages only the most important tests are mentioned, the different metals being divided into groups by what are termed *Group Tests*. The application of these will become more comprehensible by inspection of the tables hereafter introduced

BASES.

1st GROUP.

Metals which form oxides and carbonates soluble in water. The oxides are the alkalis. The hydrates and some salts exhibit an alkaline action on litmus or turmeric paper, which, however, in the case of ammonium varnishes on exposure or warming. The salts, with very few exceptions, are soluble in water and of course give no precipitate with carbonates.

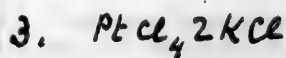
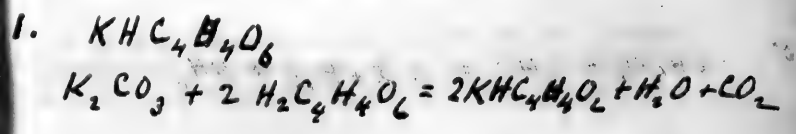
POTASSIUM.

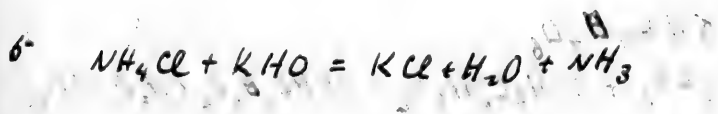
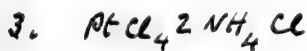
1. The hydrate or salt, if in rather strong solution, gives a crystalline precipitate when mixed with excess of tartaric acid and well shaken. When the hydrate or carbonate is used, it is necessary to fully supersaturate with the acid.

2. Hydric sodium tartrate (bitartrate of soda) may with advantage be substituted for the acid, but in that case the solutions must not be alkaline.

3. The hydrate or salt, when in not too dilute solution and acidulated with hydrochloric acid, gives a yellow precipitate with platinum tetrachloride, which is difficultly soluble in water, insoluble in alcohol.

4. Salts of potassium communicate a faint violet colour to the flame of alcohol or the blowpipe. This test is best made by heating some of the salt on a piece of clean platinum wire, or by placing the salt in a small capsule, moistening with water, adding alcohol, gently warming and inflaming.





SODIUM.

1. The hydrate or salt gives no precipitate with tartaric acid.
2. The hydrate or salt gives no precipitate with platinum tetrachloride.
3. Salts of sodium give a precipitate with potassium antimonate, but this test is not very applicable.
4. Salts of sodium communicate a bright yellow colour to the flame of alcohol or the blowpipe. The most minute trace of sodium can be detected in this way, indeed it is the only good test for this metal.

AMMONIUM.

1. Tartaric acid only forms a precipitate when the solutions employed are very concentrated, as for instance, strongest solution of ammonia, and they are violently shaken. Excess of acid must of course be added.
2. Hydric sodium tartrate produces a precipitate in not too dilute solutions.
3. Platinum tetrachloride produces a yellow precipitate in the acidulated solution.
4. Salts of ammonium are entirely volatilised by heat, and if the experiment be made in a tube, an amorphous sublimate will be found.
5. Salts of ammonium when treated with potassium or calcium hydrate evolve pungent vapours of ammonia, which form dense fumes if a rod moistened with hydrochloric acid be brought near.

 2ND GROUP.

Metals which form oxides soluble or difficultly soluble in water, and carbonates quite insoluble. They therefore form precipitates with alkaline carbonates especially after heating. The oxides are called alkaline earths. The hydrates exhibit more or less of a permanent alkaline reaction.

BARIUM.

1. The salts are precipitated *immediately* by a solution of calcium sulphate or dilute sulphuric acid. The precipitate is insoluble in all

dilute acids, but slightly soluble in boiling nitric and hydrochloric acids.

2. The salts give a precipitate with strong solution of sodium hyposulphite if violently shaken.

3. They communicate a faint greenish yellow colour to the flame of alcohol. The salt best adapted for the experiment is the chloride, which should be well moistened and warmed.

STRONTIUM.

1. The salts give a precipitate *after a time* with calcium sulphate, or, in *very dilute solutions* with sulphuric acid, in strong solutions the last re-agent produces an immediate precipitate.

2. They give no precipitate with sodium hyposulphite.

3. They communicate a beautiful crimson colour to the flame of alcohol. This is a very characteristic test.

CALCIUM.

1. Calcium sulphate produces no precipitate in salts of calcium, however concentrated the solution may be. Sulphuric acid produces no precipitate if the solution be *very dilute*, but the addition of an equal bulk of alcohol produces the precipitate. In strong solutions an immediate precipitate is formed. The above re-actions depend on the partial solubility of calcium sulphate in water and its insolubility in even weak alcohol.

2. Sodium hyposulphite produces no precipitate.

3. Oxalic acid and ammonium oxalate produce a precipitate immediately in moderately dilute, but only after a time in very dilute solutions. This precipitate is soluble in hydrochloric acid, *without* effervescence, and *insoluble* in acetic acid. If dried and heated before the blowpipe flame, it dissolves in both acids *with* effervescence.

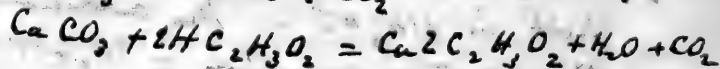
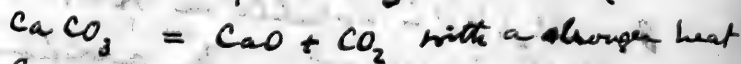
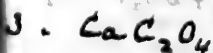
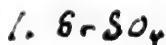
4. Salts of calcium communicate a yellowish-red colour to the flame of alcohol, somewhat resembling that produced by salts of strontium.

MAGNESIUM.

1. Calcium sulphate produces no precipitate.

2. Sodium hyposulphite produces no precipitate.

3. Ammonium oxalate produces a precipitate only in very concentrated solutions, or after a time if somewhat dilute.



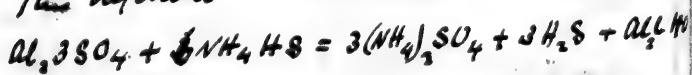
4. $\text{Inq} 2\text{H}_2\text{O}$

5. $\text{Inq} \text{NH}_4 \text{PO}_4$ when NH_3 is present - otherwise $\text{Al}_2(\text{HPO}_4)_3$

Aluminium

1. 2. $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$

This hydrate is also formed by NH_4HS :



3. $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ is soluble in H_2O but not in $\text{NH}_4\text{H}_2\text{O}$ - The addition of NH_4Cl to a solution of $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ in KHO acts thus: $\text{KHO} + \text{NH}_4\text{Cl} = \text{KCl} + \text{NH}_4\text{H}_2\text{O}$ and the Al_2O_3 being insoluble in $\text{NH}_4\text{H}_2\text{O}$ is precipitated -

4. Neutral salts are partly decomposed by ammonia giving a precipitate which is easily dissolved by ammonium chloride, or other salt of ammonia. Hence in a solution containing any ammonium salt or free acid, ammonia will produce no precipitate.

5. Sodium phosphate produces a precipitate from strong, but none from very dilute solutions. The addition of ammonium chloride and ammonia causes however a precipitate either immediately or after a time. In the latter case it is crystalline, easily soluble in acetic acid, whether crystalline or not.

3RD GROUP.

FIRST DIVISION.

Metals which form oxides insoluble in water under ordinary circumstances. Ammonium sulphide produces in solutions of their salts a precipitate which is an oxide and not a sulphide. The oxides have some tendency to unite with strong bases, such as potassa.

ALUMINUM.

1. Ammonia produces in solutions of salts of aluminum (except when certain organic bodies are present) a white precipitate, scarcely soluble in any excess of the precipitant, especially when any amount of ammonium salt is present. The precipitate is often so transparent as to be scarcely visible until allowed to settle.

2. Potassium hydrate produces a similar precipitate, readily soluble in excess of the precipitant. The solution, even if dilute, is not altered by boiling.

3. This solution in potassium hydrate is decomposed by a solution of ammonium chloride in large quantity, giving a white precipitate, but is not altered by ammonium sulphide added in small quantity.

4. The dry oxide itself, or aluminum salts, when moistened with solution of cobalt nitrate and heated, exhibits a fine blue colour. This test may be well made by adding to the solution a drop or two of cobalt nitrate, precipitating with sodium carbonate, collecting and washing the precipitate, which can then be dried and heated.

CHROMIUM.

The only salts of this metal likely to be met with are those of the sesqui or chromic oxide.

1. Ammonia produces a greenish or greyish precipitate slightly soluble in excess of the precipitant, especially after standing for some time. A pink solution is formed, from which a precipitate is produced by boiling.

2. Potassium hydrate produces a similar precipitate, easily soluble in excess, with green colour. The solution, if not very strongly alkaline, yields a precipitate on boiling.

3. This solution in potassium hydrate gives a greenish precipitate with ammonium chloride, but none with ammonium sulphide. The former re-agent should be added in excess, the latter in small quantity.

4. Salts of chromium fused with nitre in a platinum or porcelain capsule yield a yellow mass which dissolves completely in water. The solution should be divided into two parts, one yields with lead acetate a bright yellow precipitate, the other boiled with alcohol and hydrochloric acid yields a bright green solution.

5. Salts of chromium boiled with potassium hydrate and a little lead dioxide (binoxide of lead) yield a yellow solution, which may be tested as in 4.

6. The oxide communicates to a head of borax, a yellowish green colour to the inner, and an emerald green tint in the outer flame.

The higher chromium oxide will be considered under the head of chromic acid.

SECOND DIVISION.

Metals which form oxides insoluble in water under ordinary circumstances, and which are precipitated from their solutions as sulphides by ammonium sulphide. They are not precipitated from acid solutions by hydrosulphuric acid, as the sulphides are soluble in all moderately strong acids. Acetic acid will not prevent the precipitation.

ZINC.

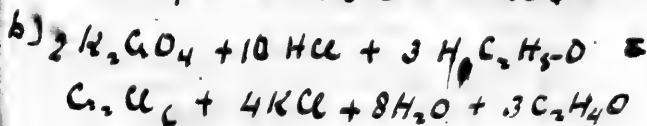
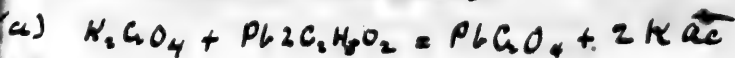
1. Ammonia produces a white precipitate, readily soluble in excess of the precipitant.



3. From the insolubility of Cr_2O_3 in NH_4OH
 $\text{KOH} + \text{NH}_4\text{Cl} = \text{NH}_4\text{OH} + \text{KCl}$



It is better to add K_2CO_3 in the large scale

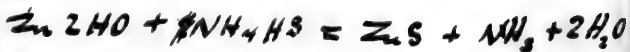


Zinc



2. $Zn 2HO$

3. (a) Ppte with NH_4HS :



No ppte because ZnO is soluble in ammonia.

Manganese

Mn 2HO

4. Mn S.

2. Potassium hydrate produces a white precipitate, readily soluble in excess of the precipitant.

3. This solution gives a white precipitate with ammonium sulphide, but none with ammonium chloride.

4. The dry oxide or salt moistened with cobalt nitrate and heated, exhibits a fine green colour. The experiment may be better made as described under aluminum.

5. The salts heated on charcoal with sodium carbonate give rise to metallic zinc, which volatilises, and by combining with oxygen forms zinc oxide, which produces on the charcoal an incrustation, yellow while hot, but white when cold.

MANGANESE.

The salts likely to occur are those of the protoxide, all the higher oxides are converted by boiling with hydrochloric acid into protochloride under evolution of chlorine, which may be recognised by its odour, or by its bleaching action on *moistened* litmus paper.

1. Ammonia produces a white precipitate, insoluble in excess, which rapidly becomes brown and even brownish-black by oxidation. If much ammonium chloride is present in the solution no precipitate will be formed at first, but a brown oxide will separate on standing.

2. Potassium hydrate acts in the same way, except that the presence of ammonium chloride does not so completely prevent precipitation.

3. Hydrosulphuric acid produces no precipitate in acid solutions, and has very little action even on neutral solutions.

4. Ammonium sulphide produces a very characteristic precipitate (manganese sulphide) of a buff or salmon colour. The tint is very easily altered by slight impurities, and the true colour obtained only from perfectly pure salts. The precipitate oxidises in the air, turning brown, and is easily soluble in acids.*

5. Compounds of manganese free from chloride when boiled with red lead and nitric acid, also free from chlorine, communicate to the solution a fine purple colour, which becomes apparent on allowing the lead oxide to settle.

* In trying the action of acids on precipitated sulphides, the precipitate should be allowed to settle, the liquid poured off, water added, and this repeated several times; or perhaps it might be better to collect on a filter and wash with distilled water.

6. Compounds of manganese fused with sodium carbonate on platinum foil in the outer flame of the blowpipe, produce a green colour owing to the formation of sodium manganate. The addition of a little nitre assists the action, as is also the case with borax. In making this experiment a very small quantity of the manganese compound should be used, as otherwise the colour appears almost black.

7. Beads of borax and microcosmic salt dissolve manganese compounds, producing a violet coloured glass in the outer flame, which becomes colourless in the inner. The addition of a particle of tin foil assists the action of the reducing flame.

IRON.

SALTS OF THE PROTOXIDE.

FERROUS SALTS.

1. Ammonia or potassium hydrate produces a precipitate which is nearly white in pure salts, but generally greenish, dirty green, or dark green; turning to black, and lastly to reddish brown by exposure to the air. Salts of ammonia prevent the precipitation by potassa partly, and by ammonia entirely.

2. Hydrosulphuric acid produces no precipitate in acid or neutral solutions.

3. Ammonium sulphide produces a black precipitate, or a green colouration if the solution be *excessive* dilute. The precipitate is easily soluble in acids.

4. Potassium ferrocyanide produces a pale blue precipitate which becomes rapidly dark blue.

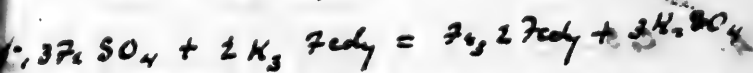
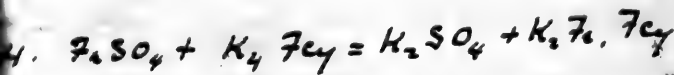
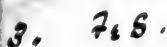
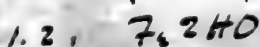
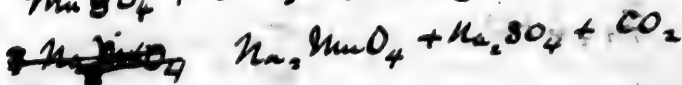
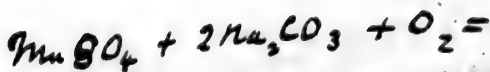
5. Potassium ferricyanide produces a dark blue precipitate.

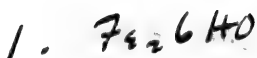
6. Potassium sulphocyanate produces no alteration if both salts be pure, the least trace of peroxide causes a reddish colour.

7. Tannic acid or infusion of gall nuts produces little or no colour in perfectly pure solutions, generally a blue tinge.

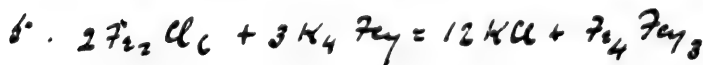
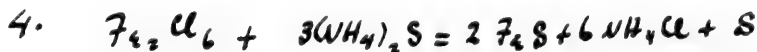
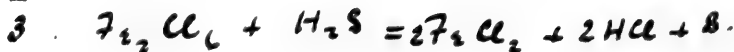
8. A bead of borax is coloured dark red by compounds of iron in the oxidising flame, the colour becoming bottle green in the reducing flame. The colours disappear almost entirely on cooling.

For making the above experiments a solution of ferrous sulphate should be mixed with a solution of sulphurous acid and boiled till inodorous and colourless.





2.



Cobalt



5. CoCy_2 soluble in excess of double cyanide and then. heated by acids.
But by boiling with excess of KCy and a drop of HCl to liberate HCy Cobalticyanide is formed K_3CoCy_4 and acids produce no effect.

SALTS OF THE PEROXIDE.

FERRIC SALTS.

1. Ammonia produces a reddish brown precipitate, unless when organic substances, such as tartaric acid, are present. The precipitate is insoluble in excess.

2. Potassium hydrate acts in the same manner.

3. Hydrosulphuric acid in excess produces only a milky precipitate or opalescence, owing to separation of sulphur.

4. Ammonium sulphide produces a black precipitate, or, if the solution be *exceedingly* dilute, a green colouration; the precipitate is soluble in hydrochloric acid.

5. Potassium ferrocyanide produces a dark blue precipitate.

6. Potassium ferricyanide produces a brown colouration.

7. Potassium sulphocyanate produces a blood red colour, destroyed by mercuric chloride (corrosive sublimate). In order to show the action of the mercuric salt, the colour should not be too deep. The red colour is not changed by boiling.

8. The blow-pipe tests are similar to those described for the ferrous compounds.

COBALT.

The salts of this metal are of rare occurrence, and of little importance except as pigments.

1. Ammonia (very dilute) produces a blue precipitate soluble in excess, forming a brownish solution. The presence of ammoniacal salts prevents the precipitation.

2. Potassium hydrate produces a blue precipitate, which turns dirty green on exposure and reddish on boiling.

3. Hydrosulphuric acid produces no precipitate in acid solutions.

4. Ammonium sulphide produces a black precipitate difficultly soluble in hydrochloric acid, easily soluble in nitric acid.

5. Potassium cyanide produces a brownish-white precipitate easily soluble in excess of the precipitant, especially on heating and in presence of free hydrocyanic acid. From this solution, containing potassium cobalticyanide, acids produce no precipitate, by which test cobalt is distinguished from nickel.

6. Compounds of cobalt used with borax or microcosmic salt produce, both in the inner and outer flames, beads of a splendid blue colour.

NICKEL.

This metal is of some importance, as it is largely used in the manufacture of so-called German Silver, and some of its salts have lately been introduced as medicinal agents.

1. Ammonia (very dilute) produces a green precipitate, easily soluble in excess, forming a light blue solution. Ammoniacal salts prevent the action.

2. Potassium hydrate produces a pale green precipitate insoluble in excess.

3. Hydrosulphuric acid produces no precipitate in acid solutions and only a brown colouration in neutral solutions.

4. Ammonium sulphide produces a black precipitate, difficultly soluble in hydrochloric acid, and not altogether insoluble in water containing ammonium sulphide. Hence the supernatant liquid is usually of a brown colour.

5. Potassium ferrocyanide produces a pale green precipitate.

6. Potassium cyanide produces a yellowish green precipitate, easily soluble in excess. The brown solution is decomposed by acids, giving a precipitate of nickel cyanide, herein differing from cobalt.

7. A bead of borax is coloured reddish yellow by oxide of nickel in the outer flame of the blowpipe. An addition of nitre changes the colour to purple.

4TH GROUP.

FIRST DIVISION.

Metals which are precipitated, as sulphides from acid solutions by hydrosulphuric acid and the sulphides of which are insoluble in alkalic sulphides (to any great extent).

FIRST SUB-DIVISION.

Metals which are precipitated from their solutions by hydrochloric acid under certain conditions.

LEAD.

1. Potassium hydrate produces a white precipitate, which is *slightly* soluble in excess of the precipitant. A very small quantity of the precipitate should be used for this experiment.

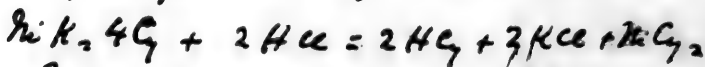
2. Ni_2HO

4. NiS .

5. Ni_2HCl

6. Ni_2Cl_2 - By x-rays NiK_2Cl_2

Reprecipitated by acids then:



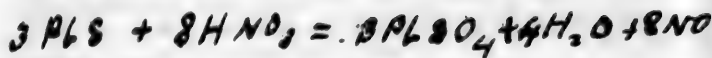
No compound ~~at~~ analogous to the Cobaltlyanide is formed.

Lead

1. Pb_2HO

2. PL_2H_2O

3. PLS



4. PLU_2

U.S. 1

5. PL_2

U.S. 1

6. PL_2O_4

U.S. 1

U.S. 1

7. $PLSO_4$

Silica

1. Ag_2O

2.

3. Ag_2S

2. Ammonia produces a similar precipitate, except in the case of the acetate, when no precipitate is formed unless a large amount of ammonia be used. The precipitate is quite insoluble in excess of ammonia.

3. Hydrosulphuric acid produces a black precipitate, insoluble in dilute acids and alkalic sulphides. The dry or elutriated precipitate is converted into white lead sulphate by boiling with nitric acid. Heated on charcoal it gives a bead of lead and an incrustation.

4. Hydrochloric acid produces a white precipitate in not too dilute solutions, which dissolves in a large excess of water especially on boiling. The solution on cooling deposits crystals. Lead chloride is therefore not entirely insoluble in water, and the metal must be looked for in dilute solutions even after the addition of hydrochloric acid.

5. Potassium iodide produces a bright yellow precipitate, soluble in a large excess of boiling water, from which it separates out on cooling in brilliant golden scales.

6. Potassium chromate produces a bright yellow precipitate, soluble in large excess of potassium hydrate. The experiment succeeds better with the nitrate than with the acetate, and also if the lead be wholly precipitated and the hydrate added rapidly.

7. Sulphuric acid produces a white precipitate almost insoluble in water and dilute acids, soluble in large excess of potassium hydrate and in ammonium acetate, also in hot hydrochloric acid.

8. Salts of lead heated on charcoal with sodium carbonate yield soft malleable globules of metallic lead, and the charcoal is covered with a yellow incrustation.

SILVER.

1. Potassium hydrate produces a brown precipitate insoluble in excess, but readily soluble in ammonia.

2. Ammonia if *very* dilute or added to an excess of the silver salt produces the same precipitate, soluble in excess of the precipitant.

3. Hydrosulphuric acid produces a black precipitate insoluble in dilute acids or alkalic sulphides, but soluble in strong hot nitric acid. The precipitate should be either dried or freed from the liquid before applying this test.

4. Hydrochloric acid produces a white curdy precipitate insoluble in acids, soluble in ammonia, potassium cyanide and sodium hyposulphite. In using the latter salt, the chloride should be precipitated by sodium chloride and not by hydrochloric acid, as, in presence of free acid, sulphur would be set free and render the solution milky.

5. Salts of silver heated on charcoal with sodium carbonate yield brilliant hard globules of metallic silver, not very malleable.

MERCURY.

MERCUROUS SALTS.

1. Potassium hydrate produces a greenish-black precipitate, insoluble in excess.

2. Ammonia produces a black precipitate, which is not the oxide but an ammoniacal compound.

3. Hydrosulphuric acid produces a black precipitate insoluble in strong nitric acid, but soluble in nitrohydrochloric acid. This sulphide is also soluble in a hot solution of potassium sulphide, metallic mercury being separated.

4. Hydrochloric acid produces a white precipitate, blackened by ammonia. This mercurous chloride, if well washed and boiled with strong hydrochloric acid, turns grey from separation of metallic mercury. The solution contains mercuric chloride. If any nitric acid be present, the whole will dissolve as mercuric chloride.

5. Potassium iodide produces a green precipitate.

6. Stannous chloride produces a white precipitate, rapidly becoming greyish black if used in excess.

7. Solutions of mercurous salts produce a grey stain on copper or gold, which volatilises by heat.

8. Heated in a tube with sodium carbonate, a ring of metallic globules is obtained. These become more distinct by rubbing them with a glass rod or piece of wood.*

SECOND SUB-DIVISION.

Metals not precipitated by hydrochloric acid.

* In making this experiment care should be taken that all moisture is excluded, as otherwise the globules are not so apparent. The carbonate should be heated strongly before use.

4. AgCl

C.N. 1

Mercurous salts

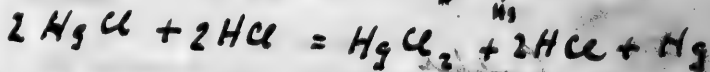
1. Hg_2O

2. With the nitrate $2(\text{NH}_2\text{Hg}_2)\text{NO}_3 \cdot \text{H}_2\text{O}$
Halim's soluble Hg_2

3. Hg_2S

Hg_2NO_3

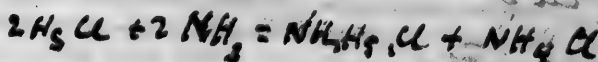
4. Hg_2Cl



5. Hg_2I

6. $\text{Hg}_2\text{Cl} \sim \text{Hg}_2$

*



Mercuric salts

1. HgO

$NH_3 Hg Cl_2$ Mercurammonium Chloride

2. ditto

3. HgS

4. HgI_2

Copper

1. $Cu.2H_2O - CuO$

2. The blue solution contains $CuSO_4 \cdot 4H_2O$

4. CuS

5. Cu_2Fe

MERCURIC SALTS.

1. Potassium hydrate added in small quantity produces a brown precipitate (oxychloride), in large quantity a bright yellow oxide. If ammonium salts be present a white precipitate is formed (mercur-ammonium chloride).

2. Ammonia produces a white precipitate of a similar nature, varying according to the character of the mercuric salt.

3. Hydrosulphuric acid added in small and gradually increasing quantities produce a white precipitate, passing into yellow, orange, brown, and lastly black. This sulphide is soluble in potassium sulphide and nitrohydrochloric acid, insoluble in nitric acid, hydrochloric acid, and ammonium sulphide.

4. Potassium iodide produces a precipitate of a yellow colour, which rapidly becomes of a brilliant scarlet, and dissolves in excess of the precipitant to a colourless solution.

5. Stannous chloride produces a white precipitate of mercurous chloride, changed by excess into grey metallic mercury.

6. Same as test 7 for mercurous salts.

7. Same as test 8 for mercurous salts.

All salts of mercury are volatile, and produce sublimes generally amorphous.

COPPER.

The only salts of common occurrence are the cupric or salts of the black oxide.

1. Potassium hydrate produces a pale blue precipitate, if excess be added and heat applied it becomes black.

2. Ammonia when dilute produces a greenish blue precipitate, easily soluble in excess forming a fine blue solution.

3. Ammonium carbonate acts in the same manner.

4. Hydrosulphuric acid produces a brownish black precipitate, soluble in hot nitric acid and not quite insoluble in ammonium sulphide.

5. Potassium ferrocyanide produces a reddish brown precipitate, insoluble in dilute acids, decomposed by potassium hydrate with separation of blue cupric hydrate, or on heating of black cupric oxide.

6. Metallic iron, when introduced into a solution of copper, especially if slightly acidulated, becomes coated with a film of red copper.

7. Any salt of copper fused on charcoal with sodium carbonate so that the melted mass sinks into the charcoal, yields brilliant red spangles of metallic copper when the fused mass is ground with a little water in an agate mortar and the liquid carefully poured off. More water can be added and the operation repeated until all the charcoal is removed.

8. Cupric oxide gives a fine green colour to a bead of borax; in the reducing flame (especially by the aid of a piece of tin foil) the bead becomes colourless while hot, but opaque red when cold. Micro-cosmic salt may also be used instead of borax.

CADMIUM.

1. Potassium hydrate produces a white precipitate, insoluble in excess.

2. Ammonia produces a white precipitate, soluble in excess.

3. Ammonium carbonate produces a white precipitate, insoluble in excess if the precipitant does not contain free ammonia.

4. Hydrosulphuric acid produces a bright yellow precipitate, insoluble in dilute acids (in the cold), ammonia or alkalic sulphides. It is soluble, however, in boiling dilute sulphuric acid, and can thus be readily separated from cupric sulphide, and detected in the solution by reprecipitation by hydrosulphuric acid.

5. Salts of cadmium reduced on charcoal by means of sodium carbonate produce a brownish yellow incrustation.

BISMUTH.

As all the salts of this metal, not containing an organic acid, are decomposed by water, it will be necessary to dissolve them by the aid of a few drops of nitric or hydrochloric acid, heat being applied. As little acid should be employed as possible, and if the original solution be diluted, a white precipitate will, in all probability, be formed, which must be re-dissolved by a little acid.

1. Potassium hydrate produces a white precipitate, insoluble in any excess.

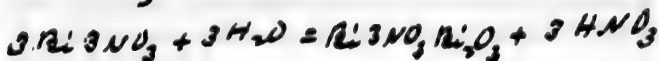
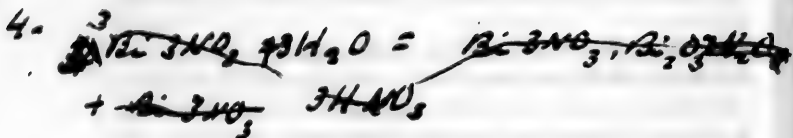
2. Ammonia produces the same.

22.51 .C

$$\begin{aligned} \text{CH}_3\text{COOH} + \text{CH}_3\text{COOH} &= \text{CH}_3\text{COOH} + \text{CH}_3\text{COOH} \\ \text{CH}_3\text{COOH} &+ \\ \text{CH}_3\text{COOH} + \text{CH}_3\text{COOH} &= \text{CH}_3\text{COOH} + \text{CH}_3\text{COOH} \end{aligned}$$

Bismuth

1.2. BiHO_2



3. Hydrosulphuric acid produces a black or nearly black precipitate, which, when dried or elutriated is soluble in nitric acid, but insoluble in alkalic sulphides.

4. Potassium chromate added in excess produces a yellow precipitate, insoluble in potassium hydrate.

5. The decomposition of salts of bismuth by water is one of the best tests. If much acid be present the solution must be evaporated to dryness and water added, a white salt will be formed which is insoluble in tartaric acid. Solutions containing a large excess of acid are not decomposed by water in any ordinary quantity.

6. Salts of bismuth treated in the usual way with sodium carbonate on charcoal by the blow-pipe flame, yield a metallic bead which falls to powder on being hammered. The charcoal acquires a yellow incrustation.

In examining the behaviour of the sulphides precipitated by hydrosulphuric acid, the precipitates must be allowed to subside, the supernatant liquid poured off, fresh water added and the operation repeated a few times; by this excess of acid will be got rid of, which in old ammonium sulphide will surely produce at least a milkiness. The metallic sulphide is then treated with ammonium sulphide (in preference to potassium sulphide which dissolves the mercurial compound).

SECOND DIVISION.

Metals which form sulphides soluble in alkalic sulphides. They may be divided into two classes.

FIRST SUB-DIVISION.

The sulphides are insoluble, and not altered by either hydrochloric or nitric acids.

GOLD.

Metallic gold is insoluble in nitric, hydrochloric, or sulphuric acid; but soluble in nitro-hydrochloric acid.

1. Salts of gold in concentrated solutions give with potassium hydrate and with ammonia a reddish yellow precipitate.

2. Stannous chloride, especially if partially oxidised, produces a purplish red precipitate or colouration.

3. Ferrous sulphate produces a brown precipitate of finely divided gold, which is blue by transmitted light if the gold solution is dilute.

4. Oxalic acid at a boiling temperature produces a precipitation of metallic gold, generally on the side of the test tube.

In employing test 3, care must be taken that no free nitric acid is present, as this of itself may produce a brown colouration with ferrous sulphate.

NOTES ON GOLD.

Articles made of tolerably pure gold are not acted on by nitric acid, while spurious or imitation gold is immediately attacked with evolution of red fumes and production of a greenish blue solution. An article may however be not pure gold, but only gilt; in that case it will be necessary to remove the outer coating before applying the nitric acid. The specific gravity also gives a tolerably fair criterion of the purity. Pure gold has a specific gravity of 19.5, jeweller's gold considerably less, varying according to purity.

Some substances are often mistaken for gold, more especially iron pyrites and golden mica. Iron pyrites in powder is attacked by hot nitric acid, with evolution of red fumes; gold is not.

The solution may be evaporated to dryness; dissolved in a little water and treated with a solution of ferrous sulphate. If gold be present in any considerable quantity a brown precipitate will be formed, but if in only minute traces a blue solution will be produced, which on standing will become colourless after a considerable time, yielding a brown precipitate.

Iron pyrites heated in the blow-pipe flame gives off sulphur which burns with a blueish light, the residual ferrous sulphide fuses and after cooling is attracted by a magnet.

Mica is quite insoluble in boiling acids.

A description of the detection of gold and silver by fluxing with lead and cupellation of the resulting button, by which process alone the presence or absence of these metals can be absolutely proved, would be foreign to the scope of this small work, and of little use to the generality of students using it.

PLATINUM.

The metal itself behaves to acids like gold.

1. Potassium hydrate acidulated with hydrochloric acid produces, in not too dilute solutions, a yellow precipitate, difficultly soluble in water and insoluble in alcohol.

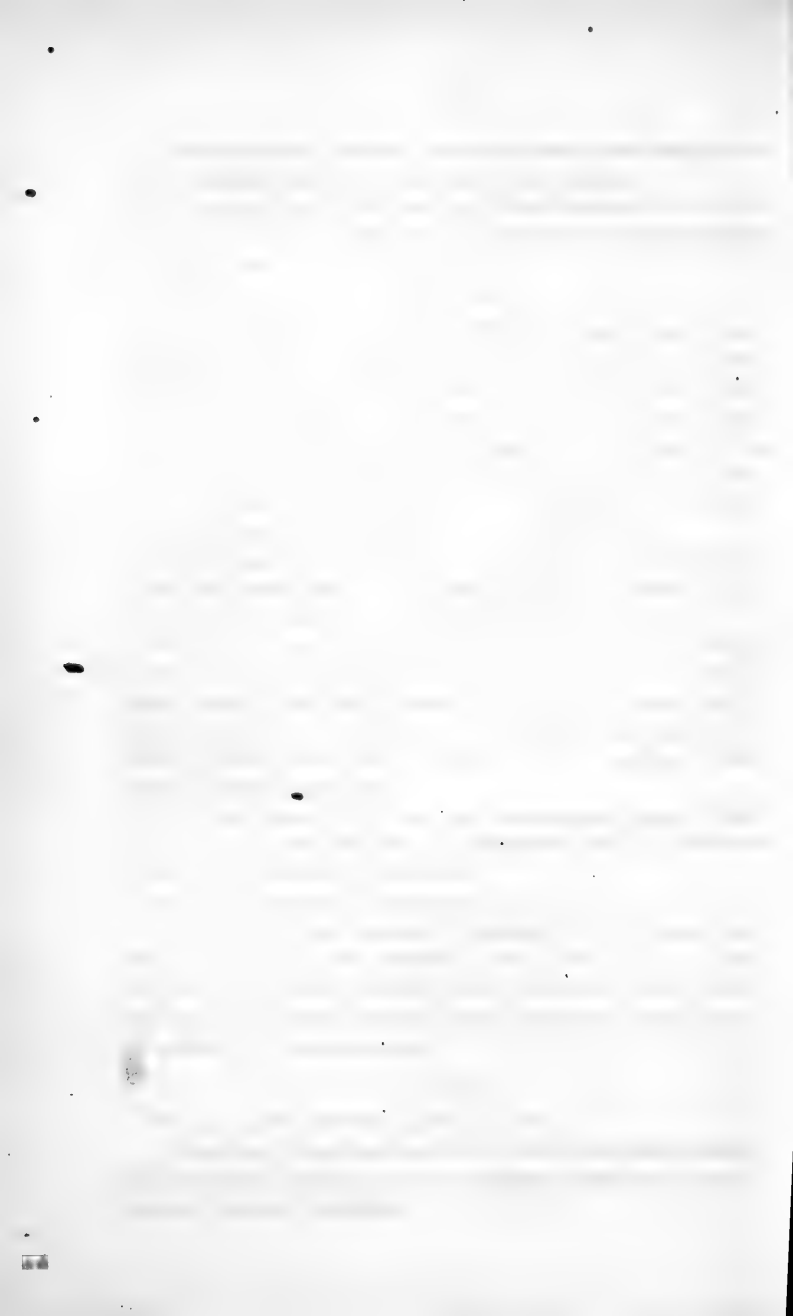
THE [illegible] OF [illegible]

BY [illegible]

IN THE [illegible] OF [illegible]

THE [illegible] OF [illegible]

IN THE [illegible] OF [illegible]



2. Ammonia acts in the same way.
3. Stannous chloride produces an intense brownish red colour.
4. Potassium iodide produces an intense brown or nearly black colour.

SECOND SUB-DIVISION.

The sulphides are either dissolved or converted into insoluble oxides by hydrochloric or nitric acid.

TIN.

STANNOUS SALTS.

Many salts of tin are partly decomposed by water.

1. Potassium hydrate produces a white precipitate, soluble in excess.
2. Ammonia produces a white precipitate, insoluble in excess.
3. Hydrosulphuric acid produces a brown precipitate, insoluble in fresh ammonium sulphide, but soluble in old sulphide or on the addition of sulphur. In this case the stannous sulphide is converted into stannic sulphide which is readily soluble.
4. Auric chloride produces a purplish red precipitate.
5. Mercuric chloride produces a grey precipitate of metallic mercury.
6. Salts of tin heated on charcoal with sodium carbonate give beads of metallic tin, intermediate in hardness between lead and silver, they are readily oxidised into white stannic oxide. The particles of tin may be separated from the charcoal as described under copper.

STANNIC SALTS.

1. Potassium hydrate produces a white precipitate, soluble in excess.
2. Ammonia produces a white precipitate, nearly insoluble in excess.
3. Hydrosulphuric acid used in excess produces a pale yellow precipitate, insoluble in dilute acids, almost insoluble in ammonia,* but easily soluble in alkalic sulphides. If dried and treated with nitric acid it is converted into stannic oxide.

* Before adding the ammonia all excess of hydrosulphuric acid must be removed, otherwise ammonium sulphide will be formed, and the precipitate dissolved.

4. Stannic salts may be reduced as in test 6 for stannous compounds.

Metallic tin is converted into white stannic oxide (metastannic acid) by the action of hot nitric acid.

ARSENIC ARSENIOUS ACID.

This substance as well as the higher oxide is ranked among the metallic oxides, as it is readily detected by the usual tests for the metals. Arsenic in its characters, however, approximates much more closely to nitrogen and phosphorus.

1. Potassium hydrate produces no precipitate.

2. Ammonia produces no precipitate.

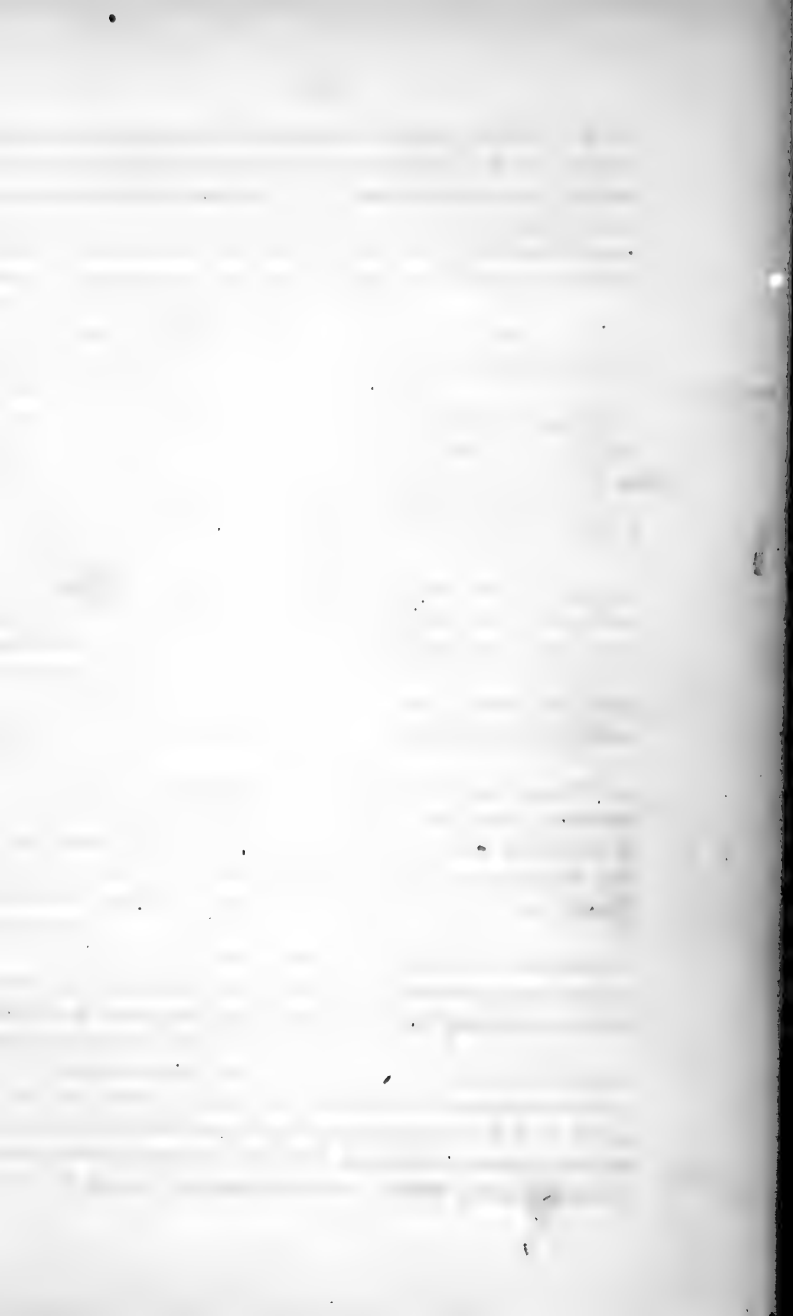
3. Hydrosulphuric acid produces in *acidulated* solution a bright yellow precipitate, insoluble in dilute acids. Easily soluble in ammonia, potassium hydrate, ammonium carbonate, and ammonium sulphide. Hereby easily distinguished from stannic sulphide and from cadmium sulphide. The solution in potassium hydrate gives on boiling with bismuth hydrate, potassium arsenite in solution and bismuth sulphide as residue. The dried yellow precipitate fused with nitre gives potassium arsenate.

4. Cupric sulphate produces little or no precipitate in a solution of arsenious acid; the careful addition of ammonia produces a bright yellowish green precipitate, readily soluble both in acids and alkalies. Hence excess of either must be avoided, and a precipitate will be at once formed if a neutral arsenite instead of the acid be used.

5. This green precipitate, if dissolved in potassium hydrate and heated, gives a fine red precipitate of cuprous oxide.

6. Silver nitrate produces no precipitate or only a faint white one in solutions of arsenious acid, the resulting arsenite being held in solution by the acid set free (the same holds in test 4). The careful addition of ammonia produces a bright yellow precipitate easily soluble in excess and also very soluble in acids, even acetic. Neutral arsenites of course produce the yellow precipitate at once.

7. Arsenious acid or any of its compounds soluble in hydrochloric acid, when boiled with a moderate excess thereof, with a piece of bright copper foil or gauze, turns the metal of a steel grey colour





from the deposition of arsenic on it, forming an alloy. If the quantity of arsenious acid present be very small the boiling must be continued for fifteen minutes, if the quantity be large the alloy soon separates off in scales. These scales or the coated copper when washed, dried and heated in a small glass tube, yield a white sublimate of arsenious acid, the octahedral form of which may readily be recognised by a magnifying glass.

The above, with the exception of the latter part of No. 7, may be called the *liquid tests* for arsenious acid; the following may be distinguished as the *dry tests*.

8. Arsenious acid (dry) heated in a tube with dry sodium acetate, evolves the horrible odour of alkarsin, the addition of stannous chloride causes the production of the still more offensive alkarsin chloride. In making this experiment, as indeed in all with arsenic, care must be taken to avoid inhaling more of the vapours than is possible.

9. Arsenious acid (dry) heated in a tube with charcoal gives rise to an easily volatile ring, of a bright metallic lustre when the arsenic is present in moderate quantity, but only brown when very minute traces are present.

10. If the tube be cut off by means of a file somewhat be^l ring, and a gentle heat applied, a very characteristic gar^l will be evolved.

11. If the tube be held in an oblique position, and a gentle heat be applied to the ring, it will sublime and form a white sublimate some distance above. In this the octahedral crystals may readily be recognised, and if obtained in sufficient quantity they may be dissolved in dilute hydrochloric acid and examined by the tests formerly described.

12. If the ring be treated with hot nitric acid it will dissolve, and if the solution be then evaporated to dryness so that all trace of nitric acid be expelled, and a drop of silver nitrate added, a brick red colour will be produced.

13. Arsenious acid or any of its salts introduced into a mixture of zinc and dilute sulphuric acid will cause the hydrogen evolved to be mixed with arseniuretted hydrogen. The gas will burn with a blueish white flame and will form dark brown metallic spots on pieces of glass or porcelain held in it. Other plans of obtaining

these deposits and methods of examining them will be detailed hereafter under the head of Poisons.

ARSENIC ACID.

1. Potassium hydrate produces no precipitate.
2. Ammonia produces no precipitate.
3. Hydrosulphuric acid, when passed into an acidulated solution for a considerable time, produces a yellow precipitate similar in most of its properties to that formed by arsenious acid. The addition of a solution of the gas will seldom produce the precipitate unless after long standing.

4. Silver nitrate produces a slight precipitate of a reddish brown colour, which is greatly increased on the addition of an alkali to neutralise the acid set free. If an arsenate be used the dense precipitate is produced at once, soluble in moderate excess of ammonia, easily soluble in nitric acid, rather difficultly soluble in acetic acid. By this reaction an admixture of an arsenate with an arsenite may readily be detected; the solution is wholly precipitated by silver nitrate, and acetic acid gradually added drop by drop. If arsenate be present a red colour will be produced.

5. Ammonia and a salt of magnesium, added to a solution of arsenic acid or an arsenate, produce a white precipitate which is crystalline when obtained from dilute solutions, easily soluble in acetic acid. In composition and properties it corresponds to the similar precipitate obtained with phosphoric acid.

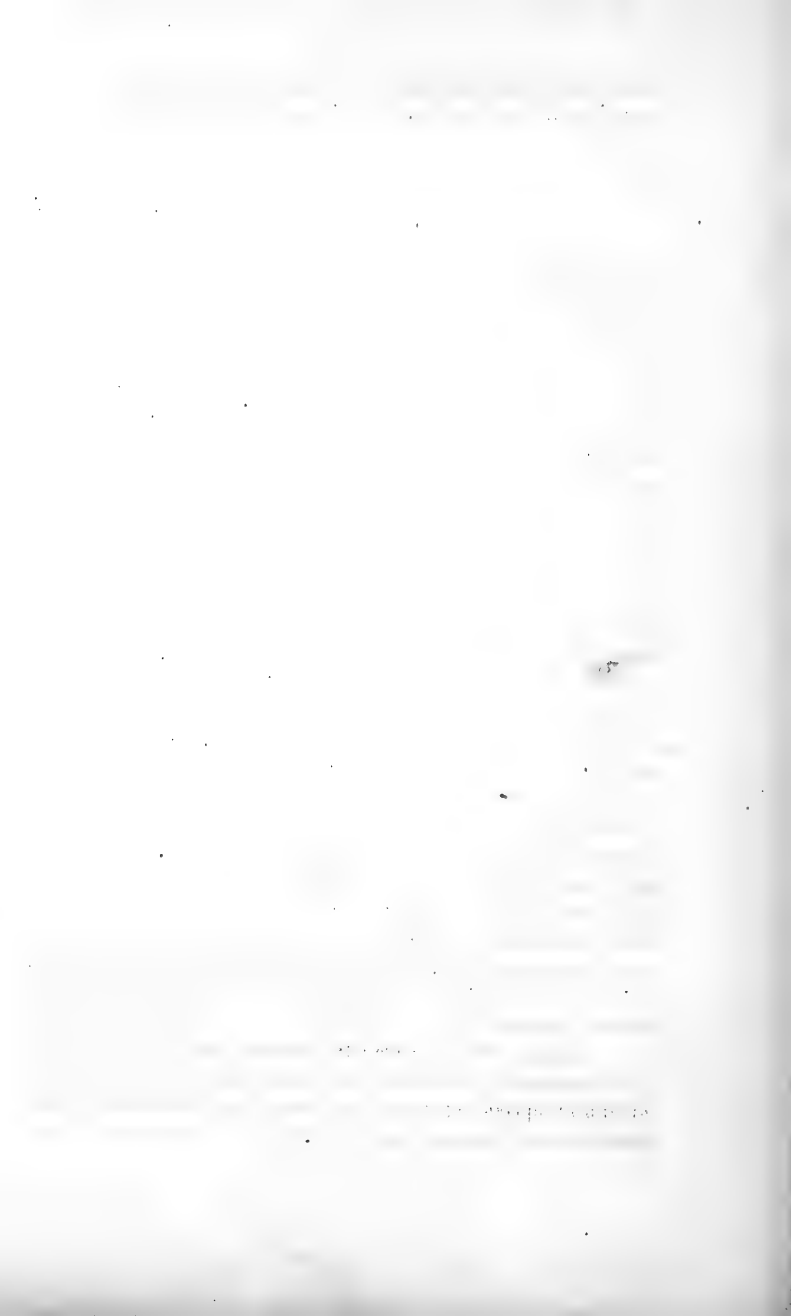
6. Arsenic acid and its salts act like arsenious acid as regards metallic copper when treated with hydrochloric acid. The acid used must however be generally stronger than in the former case.

7. Arsenic acid and its salts act in the same way as arsenious acid in presence of zinc and sulphuric acid.

8. Arsenic acid and its salts are reduced by heating with sodium carbonate and charcoal (or potassium cyanide), in the same way as arsenious acid and its salts.

ANTIMONY.

Salts of antimony not containing an organic acid are decomposed by water with formation of white basic salts soluble in acids, even tartaric. The salt commonly used for experiments is the antimonie



potassium tartrate (tartar emetic), the solution of which should be acidulated with hydrochloric acid until the precipitate first formed is re-dissolved.

1. Potassium hydrate produces a white precipitate soluble in excess.

2. Ammonia produces a white precipitate insoluble in excess.

3. Hydrosulphuric acid produces an orange red precipitate, soluble in ammonium sulphide and potassium hydrate, scarcely soluble in ammonia and insoluble in the carbonate. Boiled with potassium and bismuth hydrate it yields an alkaline solution of antimonious oxide (acid). Dried and fused with potassium or sodium nitrate it yields a mass which on treatment with water leaves an insoluble white antimonate of the base employed.

4. Zinc added to the acid solution produces a black precipitate of metallic antimony, while the gas evolved contains antimoniuiretted hydrogen.

5. Copper foil boiled with the acid solution becomes covered with a greyish black incrustation.

6. A salt of antimony added to the proper mixture for evolving hydrogen causes the evolution of antimoniuiretted hydrogen. The gas burns with a bluish white flame and deposits metallic antimony on glass or porcelain plates held over it, in the form of black velvety spots if the quantity of antimony be considerable, or in brown spots resembling those formed by arsenic if the amount be very small. The methods of distinguishing these spots from those caused by arsenic will be fully detailed hereafter.

7. Compounds of antimony fused with sodium carbonate on charcoal are reduced and form beads of metallic antimony. They are brittle, and when heated evolve white fumes of antimonious oxide, which incrust the charcoal or form prismatic crystals round the heated globule. The antimonious oxide is not nearly so volatile as arsenious acid, and usually forms prismatic but occasionally octahedral crystals.

The only preparation of antimony which may be relied upon as being entirely free from arsenic is the officinal tartar emetic.

Antimonious sulphide occurs in Canada in conjunction with galena, but the free metal itself does not occur except in minute traces. Large masses of metallic antimony, recently found in some

parts of our Dominion, may be traced to ingenious speculators, who obtained metallic antimony instead of the sulphide (known by pyrotechnists under the same name) for their experiments.

ACIDS.

1ST GROUP.

Acids which form salts, blackening more or less under the influence of heat.

OXALIC ACID.

1. Lime water and all soluble calcium salts produce with oxalic acid or its salts a white precipitate, easily soluble in hydrochloric acid without effervescence, but insoluble in acetic acid. (The chromo-oxalates are not precipitated by calcium salts; the same applies to salts containing ferric oxide or alumina.) The addition of ammonia assists the formation of the precipitate.

2. The above precipitate, if dried and heated strongly, is converted into calcium carbonate and then dissolves in hydrochloric or even acetic acid, with effervescence.

3. Dry oxalic acid or its salts effervesce when heated with strong sulphuric acid, owing to the evolution of carbon oxide and dioxide. The former can be made to burn at the mouth of the tube, with a blue flame.

4. The alkalic and earthy salts blacken slightly when heated, leaving a carbonate; under a strong heat the residue from the earthy oxalates loses carbonic acid and leaves the earth itself, showing a more or less alkaline re-action. Metallic oxalates are decomposed by heat, leaving either the oxide or the metal.

ACETIC ACID.

1. The salts of acetic acid blacken when heated but not so strongly as those of the following acids.

2. They produce no precipitates in silver or mercurous nitrates unless the solutions are rather concentrated, hence in applying group tests the solutions should be dilute.

3. Mixed with ferric chloride they give a red solution which is scarcely altered by mercuric chloride, but loses its colour under

$\frac{1}{2} \left(\frac{1}{2} \right) = \frac{1}{4}$

1. *Journal of the American Medical Association*, 1990; 263: 1025-1028.

1. *Journal of the American Medical Association*, 1997; 277: 1033-1038.

1. *Phragmites australis* (Cav.) Trin. ex Steud.

... ..

1. The first step is to identify the problem or question that needs to be answered.

1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100. 101. 102. 103. 104. 105. 106. 107. 108. 109. 110. 111. 112. 113. 114. 115. 116. 117. 118. 119. 120. 121. 122. 123. 124. 125. 126. 127. 128. 129. 130. 131. 132. 133. 134. 135. 136. 137. 138. 139. 140. 141. 142. 143. 144. 145. 146. 147. 148. 149. 150. 151. 152. 153. 154. 155. 156. 157. 158. 159. 160. 161. 162. 163. 164. 165. 166. 167. 168. 169. 170. 171. 172. 173. 174. 175. 176. 177. 178. 179. 180. 181. 182. 183. 184. 185. 186. 187. 188. 189. 190. 191. 192. 193. 194. 195. 196. 197. 198. 199. 200. 201. 202. 203. 204. 205. 206. 207. 208. 209. 210. 211. 212. 213. 214. 215. 216. 217. 218. 219. 220. 221. 222. 223. 224. 225. 226. 227. 228. 229. 230. 231. 232. 233. 234. 235. 236. 237. 238. 239. 240. 241. 242. 243. 244. 245. 246. 247. 248. 249. 250. 251. 252. 253. 254. 255. 256. 257. 258. 259. 260. 261. 262. 263. 264. 265. 266. 267. 268. 269. 270. 271. 272. 273. 274. 275. 276. 277. 278. 279. 280. 281. 282. 283. 284. 285. 286. 287. 288. 289. 290. 291. 292. 293. 294. 295. 296. 297. 298. 299. 300. 301. 302. 303. 304. 305. 306. 307. 308. 309. 310. 311. 312. 313. 314. 315. 316. 317. 318. 319. 320. 321. 322. 323. 324. 325. 326. 327. 328. 329. 330. 331. 332. 333. 334. 335. 336. 337. 338. 339. 340. 341. 342. 343. 344. 345. 346. 347. 348. 349. 350. 351. 352. 353. 354. 355. 356. 357. 358. 359. 360. 361. 362. 363. 364. 365. 366. 367. 368. 369. 370. 371. 372. 373. 374. 375. 376. 377. 378. 379. 380. 381. 382. 383. 384. 385. 386. 387. 388. 389. 390. 391. 392. 393. 394. 395. 396. 397. 398. 399. 400. 401. 402. 403. 404. 405. 406. 407. 408. 409. 410. 411. 412. 413. 414. 415. 416. 417. 418. 419. 420. 421. 422. 423. 424. 425. 426. 427. 428. 429. 430. 431. 432. 433. 434. 435. 436. 437. 438. 439. 440. 441. 442. 443. 444. 445. 446. 447. 448. 449. 450. 451. 452. 453. 454. 455. 456. 457. 458. 459. 460. 461. 462. 463. 464. 465. 466. 467. 468. 469. 470. 471. 472. 473. 474. 475. 476. 477. 478. 479. 480. 481. 482. 483. 484. 485. 486. 487. 488. 489. 490. 491. 492. 493. 494. 495. 496. 497. 498. 499. 500. 501. 502. 503. 504. 505. 506. 507. 508. 509. 510. 511. 512. 513. 514. 515. 516. 517. 518. 519. 520. 521. 522. 523. 524. 525. 526. 527. 528. 529. 530. 531. 532. 533. 534. 535. 536. 537. 538. 539. 540. 541. 542. 543. 544. 545. 546. 547. 548. 549. 550. 551. 552. 553. 554. 555. 556. 557. 558. 559. 560. 561. 562. 563. 564. 565. 566. 567. 568. 569. 570. 571. 572. 573. 574. 575. 576. 577. 578. 579. 580. 581. 582. 583. 584. 585. 586. 587. 588. 589. 590. 591. 592. 593. 594. 595. 596. 597. 598. 599. 600. 601. 602. 603. 604. 605. 606. 607. 608. 609. 610. 611. 612. 613. 614. 615. 616. 617. 618. 619. 620. 621. 622. 623. 624. 625. 626. 627. 628. 629. 630. 631. 632. 633. 634. 635. 636. 637. 638. 639. 640. 641. 642. 643. 644. 645. 646. 647. 648. 649. 650. 651. 652. 653. 654. 655. 656. 657. 658. 659. 660. 661. 662. 663. 664. 665. 666. 667. 668. 669. 670. 671. 672. 673. 674. 675. 676. 677. 678. 679. 680. 681. 682. 683. 684. 685. 686. 687. 688. 689. 690. 691. 692. 693. 694. 695. 696. 697. 698. 699. 700. 701. 702. 703. 704. 705. 706. 707. 708. 709. 710. 711. 712. 713. 714. 715. 716. 717. 718. 719. 720. 721. 722. 723. 724. 725. 726. 727. 728. 729. 730. 731. 732. 733. 734. 735. 736. 737. 738. 739. 740. 741. 742. 743. 744. 745. 746. 747. 748. 749. 750. 751. 752. 753. 754. 755. 756. 757. 758. 759. 760. 761. 762. 763. 764. 765. 766. 767. 768. 769. 770. 771. 772. 773. 774. 775. 776. 777. 778. 779. 780. 781. 782. 783. 784. 785. 786. 787. 788. 789. 790. 791. 792. 793. 794. 795. 796. 797. 798. 799. 800. 801. 802. 803. 804. 805. 806. 807. 808. 809. 810. 811. 812. 813. 814. 815. 816. 817. 818. 819. 820. 821. 822. 823. 824. 825. 826. 827. 828. 829. 830. 831. 832. 833. 834. 835. 836. 837. 838. 839. 840. 84



boiling with formation of a reddish brown precipitate of ferric oxide. This decomposition is often taken advantage of in separating ferric from manganous and other oxides.

4. Acetates heated with moderately strong sulphuric acid evolve a smell of vinegar.

5. Acetates heated with strong sulphuric acid and alcohol evolve the pleasant odour of ethyl acetate.

6. Heated with arsenious acid they evolve the horrible odour of alkarsin.

TARTARIC ACID.

1. The dry acid and its salts evolve a peculiar odour when heated somewhat resembling that of burnt sugar, blackening at the same time.

2. Calcium chloride produces in carefully neutralised solutions a white precipitate soluble in large excess of potassium hydrate, and reprecipitable on boiling.

3. Calcium hydrate must be added in large excess if the solution is not perfectly neutral in order to produce the same precipitate.

4. The acid and its salts blacken when heated with strong sulphuric acid, evolving a mixture of gases which may sometimes be made to burn at the mouth of the tube with a blue flame owing to the presence of carbon oxide.

5. The acid added in excess to potassium hydrate and well shaken produces a crystalline precipitate.

CITRIC ACID.

1. The acid and its salts blacken when heated and evolve vapours of an acid character.

2. Calcium chloride produces a precipitate after boiling.

3. Calcium hydrate gives the same reaction.

4. The acid and its salts when heated with strong sulphuric acid turn yellow and blacken only after long heating.

5. The acid gives no precipitate with potassium hydrate.

URIC ACID.

See under the heads of Urinary Calculi and Deposits.

BENZOIC ACID.

1. The acid volatilises readily evolving pungent vapours, the salts blacken and evolve generally aromatic vapours, the acid blackens only if rapidly heated.

2. Calcium chloride gives no precipitate.

3. By heating with sulphuric acid scarcely any blackening is produced as the acid volatilises.

4. Ferric chloride gives with neutral solutions a buff coloured precipitate, soluble in acids.

TANNIC ACID.

1. The acid and its salts blacken when heated.

2. The acid gives a precipitate with a solution of gelatine.

3. Ferric chloride produces a dark blue colour and precipitate.

4. Boiling sulphuric acid produces a purplish black solution, but gas is not evolved.

GALLIC ACID.

1. The acid and its salts blacken when heated.

2. The acid gives no precipitate with a solution of gelatine.

3. Ferric chloride produces a black colour and precipitate.

4. Boiling sulphuric acid acts as on tannic acid.

2ND GROUP.

Acid which form salts not blackening under the influence of heat.

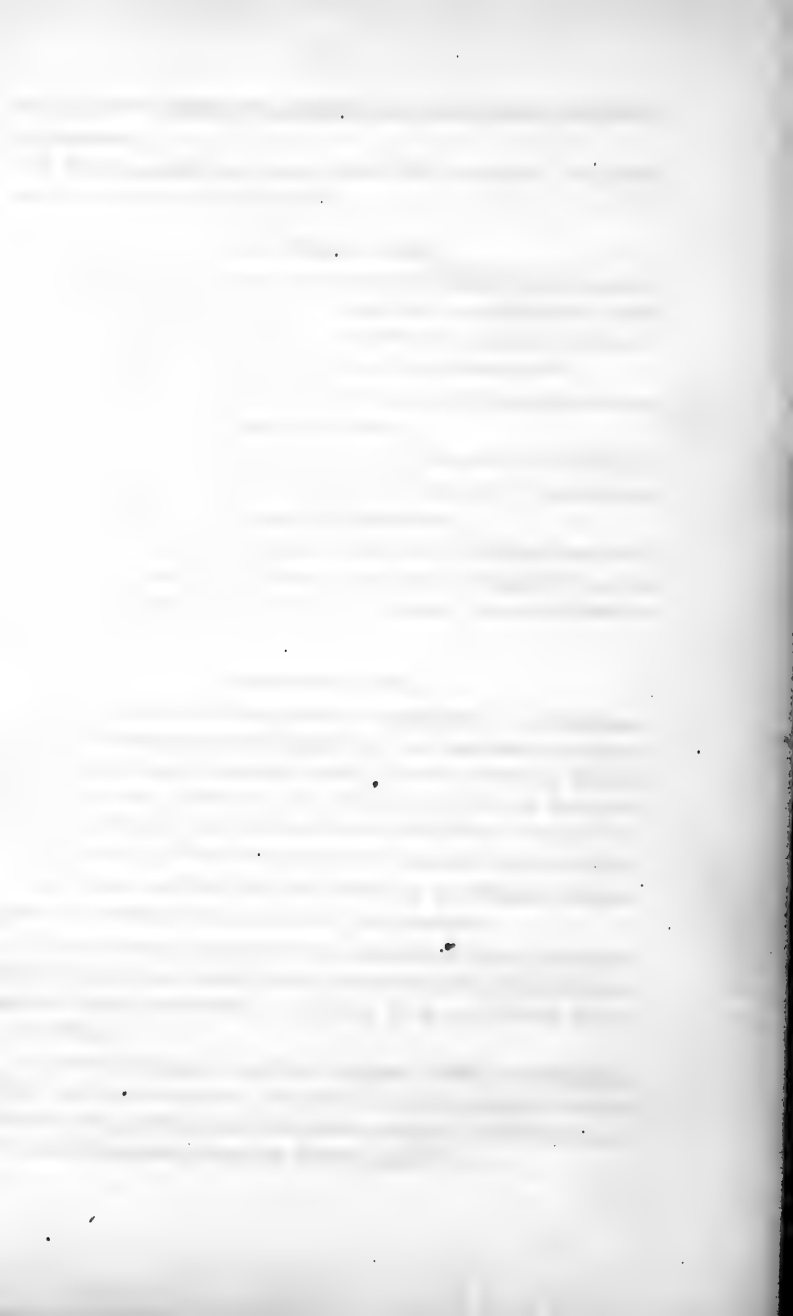
FIRST SUB-GROUP.

Neutral salts give a precipitate with barium chloride.

SULPHURIC ACID.

1. Barium chloride gives a white precipitate, quite insoluble in hydrochloric acid.

2. Sulphates heated with sodium carbonate on charcoal until fused, give a sulphide which, when moistened with water, will produce a brown stain on polished silver. The mass should be well fused until it acquires a reddish colour. A portion of it may be dissolved in water, the solution divided into two parts, one mixed with dilute sulphuric acid when hydrosulphuric acid will be evolved,





the other with sodium nitroprusside when a fine purple colour will be produced.

3. The free acid, even when dilute, will char paper if gently warmed so as to drive off the water.

SULPHUROUS ACID.

1. Sulphites give a white precipitate with barium chloride, easily soluble in hydrochloric acid. As these salts readily oxidise, they frequently contain some sulphate unless freshly prepared, in which case the precipitate is partly insoluble in hydrochloric acid.

2. Sulphites are decomposed by sulphuric acid with effervescence and evolution of gaseous sulphurous acid.

3. The gas evolved may be recognised by its smell or by its action on paper moistened with starch paste and iodic acid. Iodine is set free and produces a blue colour with the starch.

4. Sulphurous acid or sulphites mixed with hydrochloric acid and metallic zinc give rise to hydrosulphuric acid, recognisable by its smell or by its darkening action on lead paper. Stannous chloride may be used instead of zinc.

PHOSPHORIC ACID.

1. Magnesium salts do not produce a precipitate with phosphates unless the solutions are very concentrated, but if ammonium chloride and ammonia be added a white powder is thrown down only slightly soluble in water, soluble in acetic acid and insoluble in ammonia. In dilute solutions the precipitate forms only after a time or after violent shaking. When slowly formed it is granular and crystalline.

The formula is $\text{N H}^4 \cdot \text{Mg} \cdot \text{P O}^4$, the only modification of phosphoric acid which need be considered being tribasic.

2. Lead acetate produces a white precipitate which, when well washed, dried and heated in the outer blow-pipe flame fuses and becomes highly crystalline on cooling. It is not reduced by the inner flame.

3. Silver nitrate gives a yellow precipitate, easily soluble both in nitric acid and ammonia. All salts of tribasic phosphoric acid, whether they contain one, two or three atoms of fixed base, yield the same precipitate having the formula $\text{Ag}^3 \text{P O}^4$.

4. If a solution of a phosphate, which must not be strongly acid, be mixed with a considerable quantity of sodium acetate and a drop of ferric chloride be added, a yellowish white precipitate of ferric phosphate will be formed.

5. Ammonium molybdate mixed with nitric or hydrochloric acid until the precipitate first formed is re-dissolved, produces in a dilute solution of a phosphate, especially by the aid of a gentle heat, a yellow colour and yellow precipitate. The quantity of phosphate used should be small as otherwise the precipitate is dissolved.

BORACIC ACID (BORIC).

1. A concentrated solution of a borate when mixed with sulphuric acid to strongly acid reaction, deposits crystalline scales of boric acid on cooling.

2. If alcohol be added to a portion of this mixture and kindled, it will burn with a bright green flame.

3. Turmeric paper moistened with a solution of boric in hydrochloric acid acquires a bright brownish red colour, especially distinct after drying.

CARBONIC ACID (CARBON DIOXIDE).

1. The gas itself is readily detected by giving a white precipitate when shaken with lime water, excess of gas re-dissolves the salt.

2. All carbonates are decomposed by acids, with effervescence. The escaping gas is inodorous.

3. Carbonates gives precipitates with calcium and barium chlorides, easily soluble with effervescence even in weak acids.

CHROMIC ACID.

1. All the chromates are yellow, red or brown.

2. The solutions when strongly acidified are reduced by hydrosulphuric acid if added in large excess. The solution becomes of a green colour and milky from separation of sulphur. The test will not succeed unless the hydrosulphuric acid is freshly prepared and used in great quantity.

3. Chromates are reduced by boiling with alcohol and hydrochloric acid, a bright green solution being produced, in which the presence of chromic oxide may be detected (chromium).

4. Soluble chromates give a yellow precipitate with soluble lead salts, the precipitate is soluble in large excess of potassium hydrate (lead).

5. Chromates heated with dry or fused sodium chloride and strong sulphuric acid, evolve dark red fumes of chromium oxychloride. The vapours if conducted into a solution of ammonia will form a yellow solution.

SILICIC ACID.

1. Hydrochloric acid causes, in strong solutions of silicates, the separation of a gelatinous hydrate. In weak solutions the acid remains dissolved, but becomes insoluble in water, and all acids (except hydrofluoric) on evaporating to dryness.

2. To detect the acid in insoluble silicates, the substance in fine powder must be fused with four parts of sodium carbonate, the fused mass dissolved in water, hydrochloric acid added, evaporated to dryness, moistened with acid and washed with water. A white residue indicates silicic acid.

3. The finely divided acid will dissolve in boiling potassium hydrate or sodium carbonate.

4. Fused with sodium carbonate it dissolves with evident effervescence forming a clear bead.

ARSENIOUS ACID.

ARSENIC ACID.

ANTIMONIC ACID.

See under Arsenic and Antimony.

HYDROFLUORIC ACID.

1. All soluble fluorides give a precipitate with neutral calcium chloride, insoluble in acetic acid.

2. All fluorides when fused with hydric potassium sulphate evolve the above acid which acts upon glass.

3. Most fluorides when treated with strong sulphuric acid evolve hydrofluoric acid which acts on glass.

4. Fluorides when mixed with silica and treated with strong sulphuric acid evolve silicon tetrafluoride which, in contact with water, is decomposed, depositing gelatinous silica and forming a solution of hydrofluosilicic acid.

IODIC ACID.

1. Salts of this acid give a precipitate with barium chloride.
2. The salts are reduced by sulphurous acid with separation of iodine which may be recognised by its action on starch.
3. Iodates deflagrate when heated on charcoal, evolving violet fumes of iodine. Hence this acid belongs partly to Group III.

SECOND SUB-GROUP.

Neutral salts give no precipitate with barium chloride, but one with silver nitrate.

HYDROCHLORIC ACID. (CHLORINE.)

1. Silver nitrate produces a white curdy precipitate which separates readily on violent agitation, insoluble in nitric acid, soluble in ammonia, blackening by exposure to light.
2. Chlorides treated with moderately strong sulphuric acid evolve pungent fumes of hydrochloric acid, producing a dense smoke in presence of ammonia. The gas evolved does not bleach.
3. Chlorides heated with manganese dioxide and moderately strong sulphuric acid evolve chlorine, recognisable by its odour and by its bleaching action on moist litmus paper. The acid used should be made of about equal parts strong acid and water.
4. Chlorides heated with potassium chromate and strong sulphuric acid evolve dark red fumes (page 49), soluble in ammonia with a yellow colour.

HYDRIODIC ACID (IODINE).

1. Silver nitrate produces a pale yellow precipitate insoluble in nitric acid and in ammonia, by which latter re-agent the colour generally becomes lighter. In trying the action of nitric acid, it is necessary to be careful that the iodide has been fully decomposed by the silver salt, as in presence of free iodide a brown colour or precipitate will be caused from separation of iodine.
2. Fuming nitric acid or solution of chlorine will produce in strong solutions a brown precipitate if added in sufficient quantity. An excess of the latter re-agent will dissolve the precipitate, forming a colourless solution; hence the use of chlorine is objectionable where only traces of iodine are present. In such cases tests 5 and 6 may be employed.



3. In very dilute solutions only a yellow colour will be produced. That this arises from free iodine may be proved by shaking the solution with a few drops of chloroform or carbon disulphide, which liquids absorb the iodine and sink to the bottom with a fine pink colour, or dark red if much iodine is present. Benzoline or light petroleum oil may be used, but these of course float on the top.

4. A small quantity of starch paste added to the yellow solution will produce a blue colour. It is to be remembered that the iodine must be in a free state.

5. The best method of using the starch test is to add the paste and a few drops of hydrochloric acid to the solution of iodide, and then one drop of solution of potassium chromate. A blue colour will be produced immediately or after a time, even when the amount of iodine is exceedingly small.

6. Instead of chlorine water for setting free the iodine, a solution of nitrous in sulphuric acid may be advantageously used. The solution is obtained by passing the vapours evolved from a heated mixture of starch and nitric acid through common sulphuric acid. This re-agent has the advantage that it decomposes iodides, but has no action on chlorides and bromides.

7. A dry iodide heated with strong sulphuric acid, with or without manganese dioxide, will evolve violet fumes of iodine.

8. Lead acetate produces a bright yellow precipitate (page 33.)

9. Palladium chloride produces an intense brown or black colour and precipitate with very dilute solutions of iodides.

HYDROBROMIC ACID (BROMINE).

1. Silver nitrate produces a pale yellow precipitate very little soluble in ammonia, unless used in large excess and on application of heat.

2. Dry bromides heated with moderately strong sulphuric acid, with addition of manganese dioxide, evolve brownish yellow vapours of bromine, recognisable by their smell and bleaching action on moistened litmus paper. The vapours may be distinguished from those of chromium oxychloride, which they somewhat resemble, by passing them into ammonia, with which they form a colourless solution.

3. Bromine may be set free from its compounds by chlorine or by hydrochloric acid and potassium chromate, and if starch be added a yellowish or slightly reddish colour is communicated to the starch. This test is often not very satisfactory, but succeeds much better if made in the manner recommended by Fresenius. The bromide with manganese dioxide and sulphuric acid is placed in a very small beaker, covered by a plate or watch glass on which has been fastened a piece of paper smeared with starch paste with some dry starch sprinkled over it. On warming gently and standing, a fine reddish yellow colour is produced, the dry starch being bright red if any quantity of bromine be present.

HYDROCYANIC ACID (CYANOGEN).

1. Silver nitrate produces a white precipitate, soluble in ammonia, but insoluble in dilute nitric acid. The dried cyanide when heated in a tube is decomposed giving off cyanogen which may be made to burn at the mouth of the tube with a pink coloured flame, the residue is metallic silver, easily soluble in nitric acid. By very long boiling in nitric acid the cyanide is dissolved.

2. If this precipitate be collected on a filter, washed, dried and then introduced into a narrow quill tube in which a small fragment of iodine has been previously placed, on gently heating the iodine, beautiful acicular crystals of cyanogen iodide will be formed somewhat above the cyanide. The heat must be very moderate.

3. If to a solution of ferrous sulphate (or chloride) mixed with a few drops of ferric chloride, hydrocyanic acid or a cyanide be added, and then potassium hydrate, a dirty green or dark precipitate will be formed, which on the addition of hydrochloric acid forms a dark blue liquid, from which a precipitate of the same colour gradually subsides. If the amount of hydrocyanic acid is *very* small, the solution is rather green than blue, and deposits a blue precipitate only after long standing.

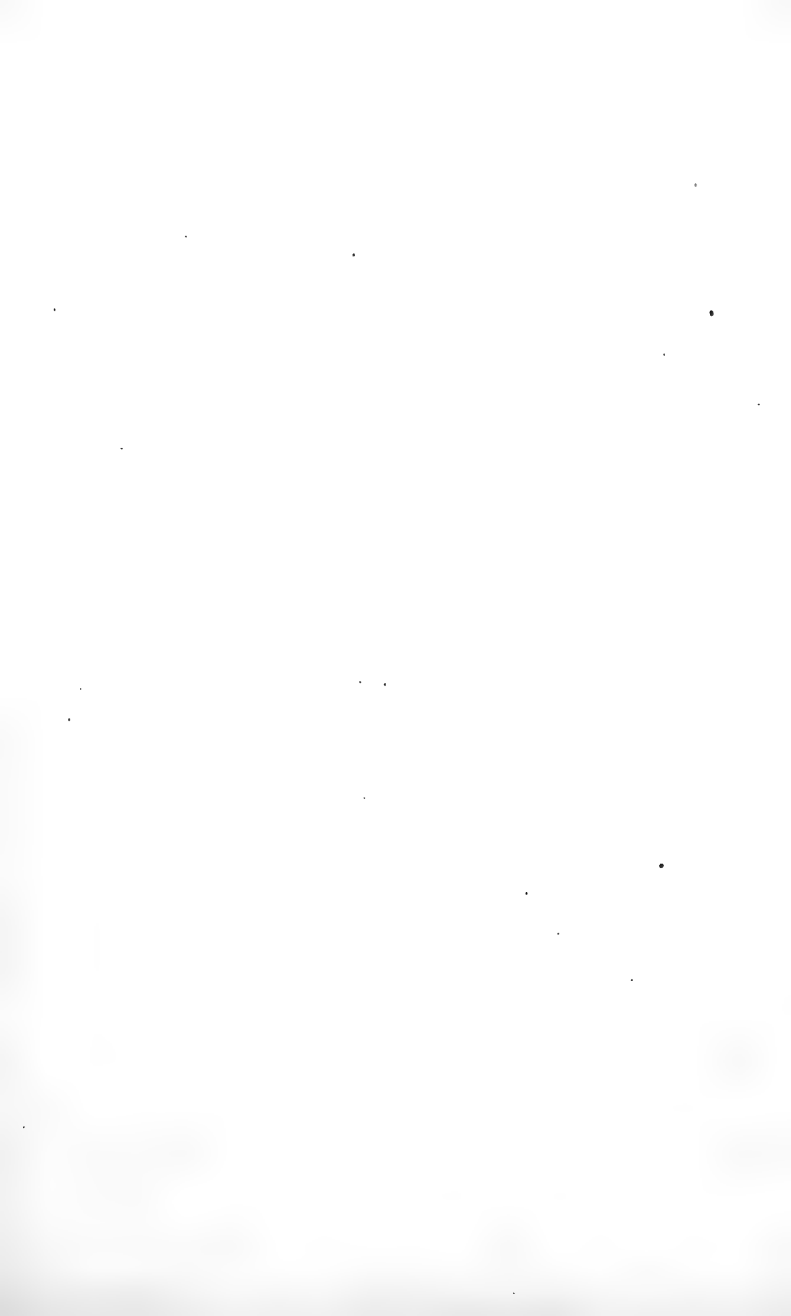
4. If hydrocyanic acid be mixed with a few drops of yellow ammonium sulphide, and boiled till *perfectly* inodorous, or evaporated to dryness, ammonium sulphocyanate will be produced, which gives with ferric chloride a blood red colour, destroyed by excess of mercuric chloride. The experiment is best made in a porcelain capsule.

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5. Hydrocyanic acid is readily evolved from most of its compounds by moderately strong sulphuric acid, and is easily recognised by its odour. It is scarcely necessary to mention that caution is here required, the acid being so exceedingly poisonous.

Other methods of testing for this acid will be given under the chapter on Poisons.

HYDROSULPHURIC ACID (SULPHUR).

1. Soluble and many insoluble sulphides are decomposed by dilute sulphuric acid with effervescence, the gas escaping is hydro-sulphuric acid recognisable by its peculiar odour, somewhat resembling that of rotten eggs, by its burning with a blue flame, and by its darkening action on lead paper.

2. Soluble sulphides give a magnificent purple colour with sodium nitro-prusside and a black precipitate with lead salts.

3. Many metallic sulphides when heated in a tube, open at both ends, and held in an oblique position, give off fumes of sulphurous acid, recognisable by their odour, and their action on paper soaked in a mixture of iodic acid and starch paste (page 47.)

4. Sulphides when treated with strong nitric acid, cause red fumes to be evolved, a yellow substance (sulphur) is often separated, and the resulting solution is found to contain sulphuric acid; before the addition of the barium salt, the solution must be largely diluted.

HYDROFERROCYANIC.

1. Ferric chloride gives a dark blue precipitate.

2. Ferrous chloride or sulphate gives a pale blue precipitate.

3. The solutions of ferrocyanides are usually turned blue by the addition of strong acids.

4. Silver nitrate produces a whitish precipitate, insoluble in nitric acid.

HYDROFERRICYANIC.

1. Ferric chloride gives a brown colour.

2. Ferrous chloride or sulphate gives a dark blue precipitate.

3. Silver nitrate produces a yellowish red precipitate, insoluble in nitric acid.

SULPHOCYANIC.

1. Ferric chloride produces a blood-red colour, not altered by boiling, but destroyed by mercuric chloride in excess.

2. Ferrous chloride or sulphate, if pure, produces no change of colour with pure sulphocyanate.

3. Silver nitrate produces a whitish precipitate, insoluble in nitric acid.

GROUP III.

Acids the salts of which give no precipitate with either barium chloride or silver nitrate, do not blacken when heated on charcoal, but produce deflagration.

CHLORIC ACID.

1. Chlorates give no precipitate with calcium or barium salts; they give no precipitate with silver nitrate if quite pure, unless previously heated so strongly that effervescence takes place. By this oxygen is evolved and a chloride remains.

2. Chlorates deflagrate violently when heated on charcoal.

3. Chlorates heated with strong sulphuric turn yellow and evolve a gas which explodes violently. This experiment must be made with care.

4. In solutions acidulated with sulphuric acid, chlorates will destroy the blue colour of solution of indigo on application of heat.

NITRIC ACID.

1. Nitrates if pure give no precipitate with dilute calcium barium or silver salts.

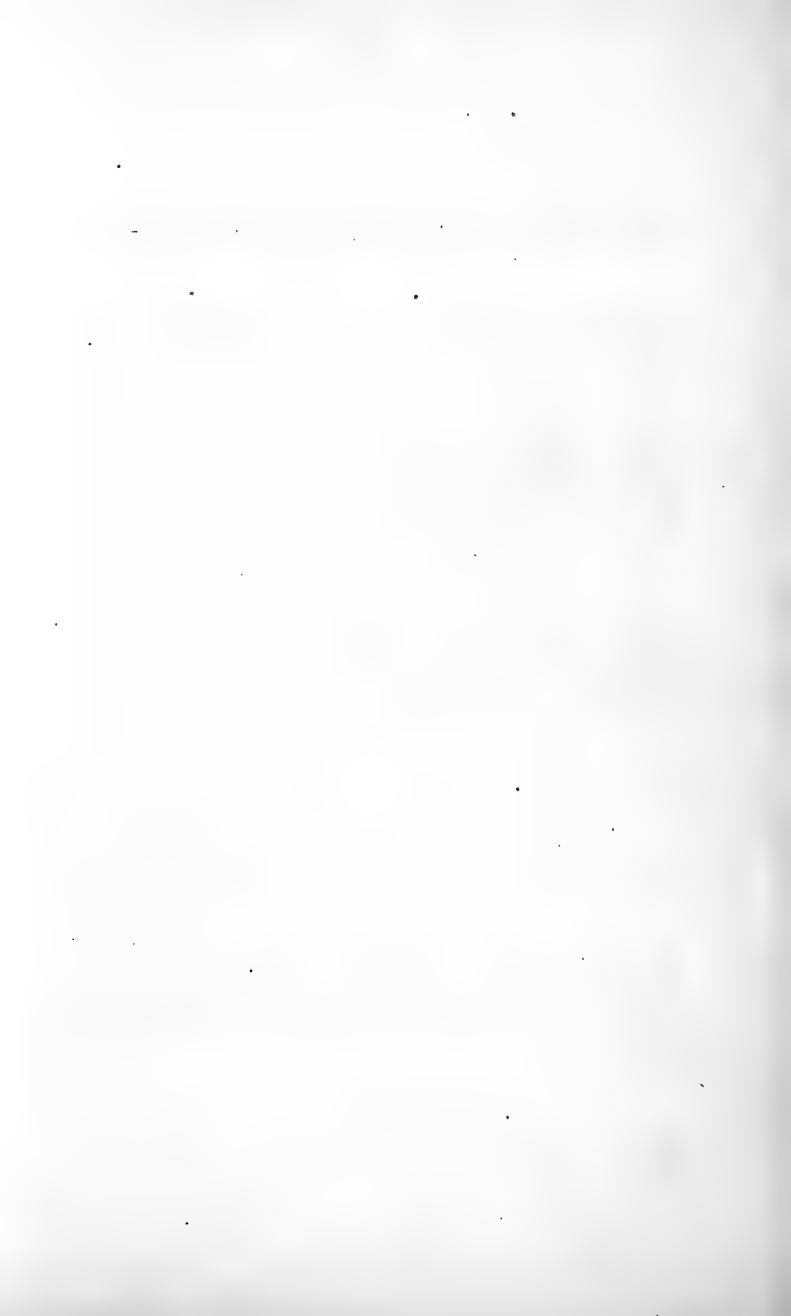
2. Nitrates deflagrate when heated on charcoal.

3. Heated with sulphuric acid and a little metallic copper they evolve red fumes.

4. In solutions acidulated with sulphuric acid, all nitrates destroy the blue colour of solution of indigo on application of heat.

IODIC ACID

Has been already treated of in Group II.; it belongs partly to Group III.



PLAN FOR DETECTING THE METAL IN A SUBSTANCE SOLUBLE
IN WATER, AND CONTAINING NOT MORE THAN ONE BASE
AND ONE ACID.

A rather strong solution of the substance is made, care being taken that the whole is dissolved; the test tube containing this *original solution* should be always placed in a certain part of the test tube stand, say in the left hole of the upper row.

A portion of this being diluted with water is tested with $H\ Cl$. If a precipitate is formed the acid is added until no further deposit results, and a slight excess added. If no resolution takes place, the base belongs to Group I; if no precipitate is formed, or if it is re-dissolved, pass on to Group II, adding to the *same* solution a *large* quantity of hydrosulphuric acid.

If no precipitate is formed, or only a milky opalescence, pass on to Group III, adding to the *same* solution a considerable quantity of ammonium chloride, ammonia till the liquid after being well shaken smells strongly, and then whether a precipitate has been formed or not, a small quantity of ammonium sulphide.

If no precipitate is formed pass on to Group IV, adding to the *same* solution sodium carbonate.

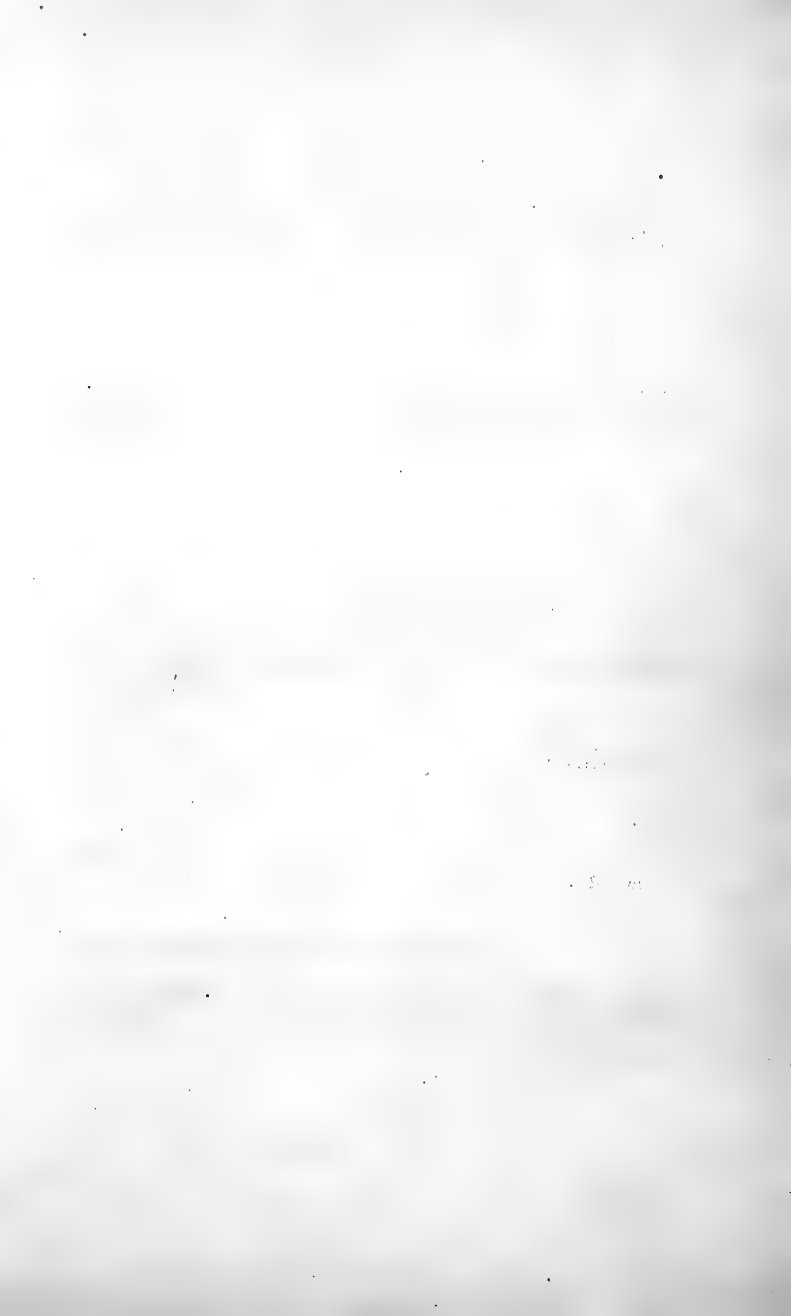
If no precipitate is formed the base must come under Group V, or perhaps there may be no base present.

Having thus brought the base into the proper group, proceed according to the several tables.

NOTE.—In some cases a clear crystalline salt may refuse to dissolve in water, becoming opaque (bismuth, antimony, tin), changing colour (mercury) and leaving a sediment quite insoluble in hot water, in such cases nitric or hydrochloric acid should be carefully added, with application of heat, until a clear solution is obtained. As little acid as possible should be used.

GROUP TABLE FOR BASES.

| I.
H Cl produces a precipitate in-soluble in excess. | II.
H ² S in excess forms a precipitate. | III.
After addition of N H ⁴ Cl and neutralization by N H ³ , (N H ⁴) ² S produces a precipitate. | IV.
Sodium carbonate produces a precipitate. | V.
No precipitate by any of these re-agents. |
|--|---|---|---|---|
| The solution should not be very concentrated, as H Cl will precipitate Ba Cl ² from strong solutions. | Soluble in (N H ⁴) ² S
Pt—black
Au—black
Sn—pale yellow
(Stannic sulphide)
As—yellow
Sb—Orange | Fe—black
Co—black
Ni—black
Mn—buff
Zn—white
Al—white
Cr—greenish | Ba—white
Sr—white
Ca—white
Mg—white | K
Na
N H ⁴ |
| Tartar emetic will give a precipitate with H Cl soluble in excess. | Soluble in (N H ⁴) ² S with S added
Sn—brown
(Stannous sulphide)
Insoluble in (N H ⁴) ² S | The colour of the Mn S is often not clear buff, and of the Zn and Al often dirty white. The precipitate with Al is often not very visible until after standing. | | |
| Ag
Pb
Hg in mercurous salts. | Pb—black
Cu—black
Hg—black
Bi—brown-black
Cd—yellow
Lead is included in this group, as the chloride is not quite insoluble in water. | | | |



GROUP I.

Ammonia added to the white precipitate formed by hydrochloric acid.

Dissolves it.

Ag

Turns it black.

Hg

Leaves it almost unchanged.

Pb

In these, as in all other cases, the student should make several confirmatory tests to arrive at perfect certainty, and never depend on one test alone.

GROUP II.

A The precipitate is soluble in $(\text{NH}^+)^2\text{S}$, especially on addition of powdered sulphur.

| Black. | | Brown. | Orange. | Yellow. | |
|--|---|------------------|---------|--------------------------|----------------------------|
| Original solution with HCl and KCl gives yellow precipitate. | Original solution with FeSO_4 gives brown precipitate. | | | Soluble in NH_3 | Insoluble in NH_3 |
| Pt | Au | Sn
(Stannous) | Sb | As | Sn
(Stannic) |

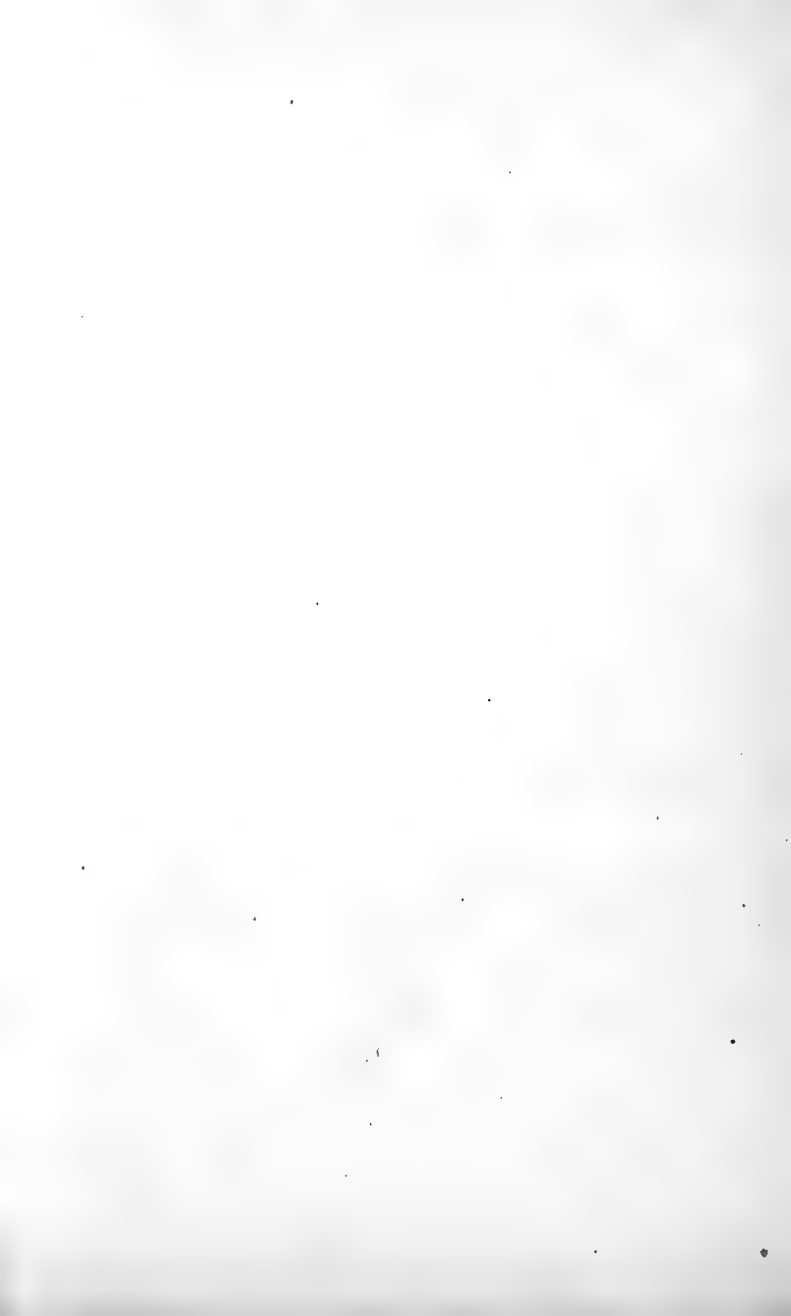
B The precipitate is insoluble in $(\text{NH}^+)^2\text{S}$.

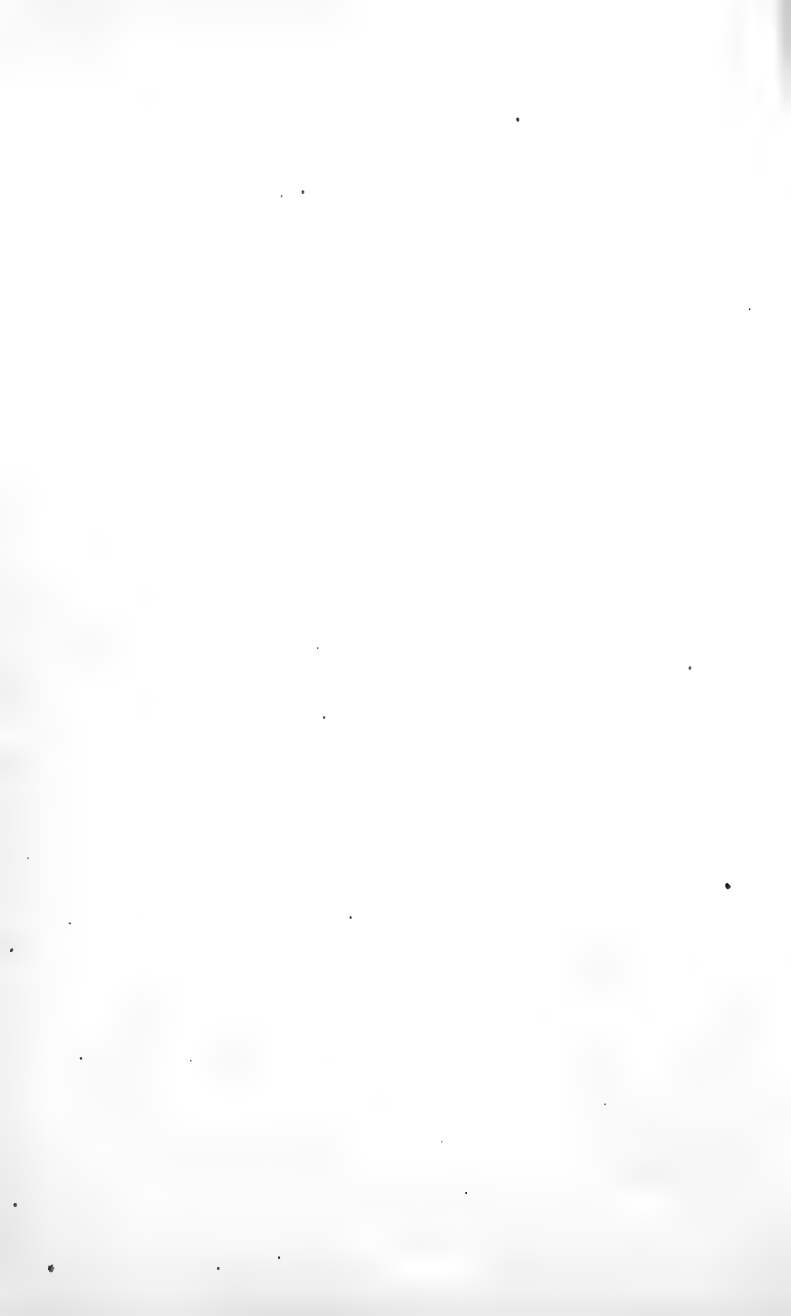
| | | | | |
|---------|--|--|--|---|
| Yellow. | Original solution gives white precipitate with H^2SO_4 | Original solution gives yellow precipitate with KHO | Original solution gives blue colour with NH_3 | Original solution gives yellow precipitate with K^2CrO_4 , insoluble in KHO . Salts decomposed by H^2O |
| Cd | Pb | Hg
(Mercuric) | Cu | Bi |

GROUP III.

| N H ⁴ : S produces | | | | |
|---|--|--|--|---|
| A black precipitate which when washed is | | A buff precipitate | A green precipitate | A white precipitate |
| Soluble in H Cl | Insoluble in H Cl | Soluble in H Cl | Soluble in H Cl | Soluble in H Cl |
| Original solution gives with K H O a dirty green or brown precipitate | Original solution gives with K H O a green ppte. | Original solution gives with K H O a white precipitate turning brown | Original solution gives with K H O a green precipitate soluble in excess | Original solution gives with N H ₃ a ppte. insoluble in excess |
| Fe | Ni | Mn | Cr | Zn |
| | Co | | | Al |

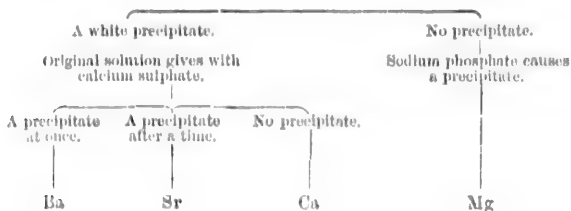
The precipitated sulphide must be well washed before trying its solubility in H Cl; the manganese sulphide may not exhibit a pure buff or salmon colour, the white precipitates of zinc sulphide and alumina may from presence of impurities be of a dirty or greenish colour. Hence the above tests and others should be applied to the original solution or the blow-pipe and fusion tests to the dry substance. In acid solutions, containing no metals forming dark coloured sulphides, earthy phosphates and oxalates may be present, precipitated both by ammonia and ammonium sulphide. The precipitates are more or less white, and may be examined as described at a subsequent page.





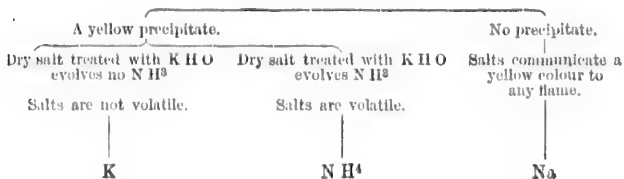
GROUP IV.

The original solution mixed with ammonium chloride and carbonate gives :



GROUP V.

Original solution acidulated with hydrochloric acid gives with platinum tetrachloride :



**PLAN FOR THE DETECTION OF THE ACID OR HALOGEN IN A
SALT SOLUBLE IN WATER, AND CONTAINING NOT MORE
THAN ONE BASE AND ONE ACID.**

It is not possible to draw out so simple a plan for the detection of the acids as for that of the bases, some of them coming under several groups. Two tables have been constructed, in the first arsenious, arsenic, antimonious and chromic acids have been omitted, as they must have been detected during the previous examination for bases. In using the second table the student must remember that for each column a *fresh* portion of the original solution must be employed, and the group tests applied in succession, whatever may have been the result obtained in the previous experiments, excepting when sulphuric acid has been found in the first trial.

Confirmatory tests must in every instance be resorted to, and the determination of the base previously will render the search for certain acids in a soluble salt unnecessary. Thus heavy metallic oxides or earths would prevent the presence of carbonic and many other acids which form insoluble salts. Barium, strontium and calcium, in an easily soluble salt, would prevent the presence of sulphuric acid, silver and lead of chlorine, iodine and bromine, and so on. When an alkali has been found, all acids may be present.

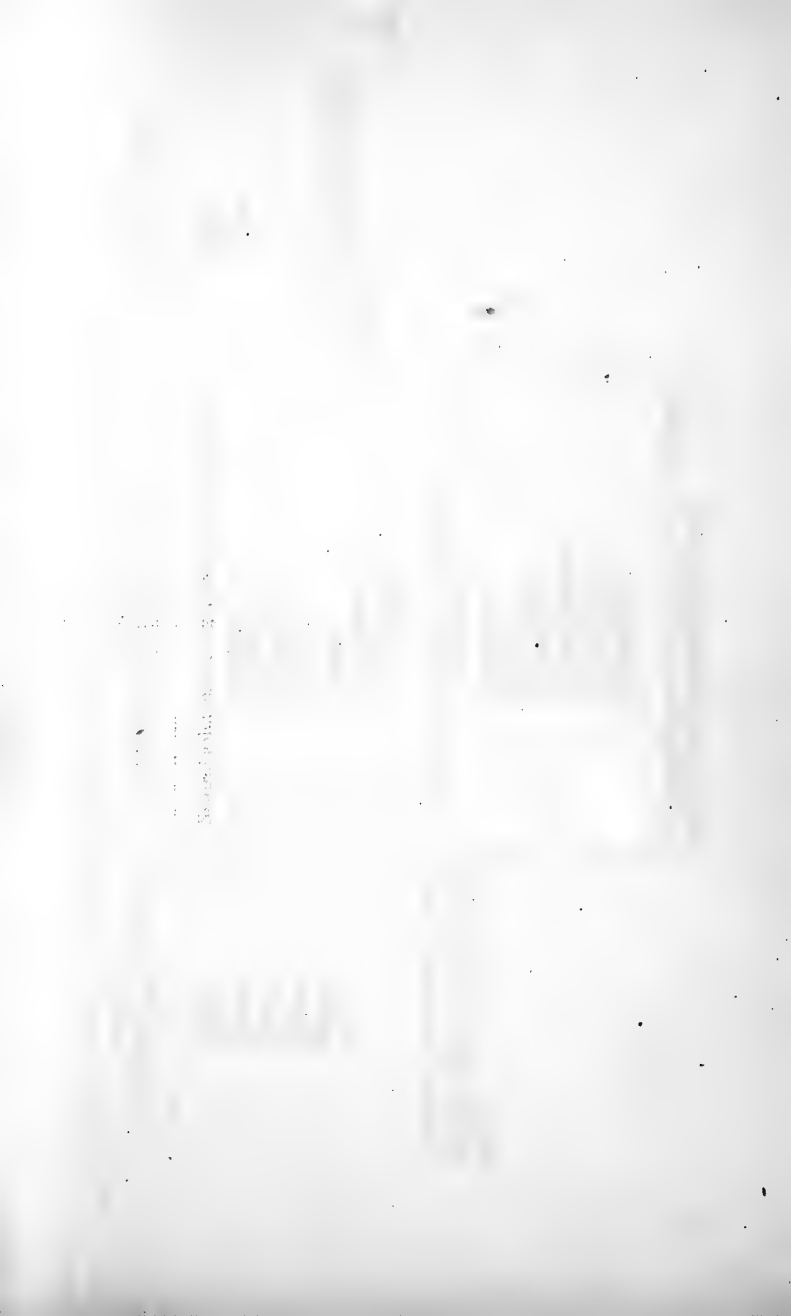




TABLE I.

| GROUP I.
The salts are more or less blackened when heated. | GROUP II.
Salts not blackened by heating nor deliquescent on charcoal. | GROUP III.
Salts not blackened by heating, but deliquescent on charcoal. |
|--|--|--|
| <p>Oxalic
Acetic
Tartaric
Citric
Uric
Benzoic
Tannic
Gallic</p> <p>Many oxalates blacken only very slightly, and the acid itself will volatilise without giving any dark colour.</p> | <p>Neutral solutions giving a precipitate with Ba Cl_2</p> <p>Sulphuric
Sulphurous
Phosphoric
Boric
Silicic
Carbonic
Hydrofluoric
(Oxalic) 1st Group
(Iodic) 3rd Group.</p> <p>Neutral solutions giving no precipitate with Ba Cl_2 but with Ag N O_3</p> <p>Hydrochloric
Hydriodic
Hydrobromic
Hydrocyanic
Hydroferrocyanic
Hydroferriocyanic
Hydrosulphuric
Sulphocyanic</p> <p>The metallic acids alluded to on the last page would come into the first division of this group.</p> | <p>Chloric
Iodic
Nitric</p> <p>Perchloric and bromic acids would fall into this group, but are of rare occurrence.</p> |

1st GROUP.

| Reddened when heated to dryness
with H N O_3 | When heated with $\text{H}^2\text{S O}_4$ | Giving black or dark colour with
ferric chloride | When heated evolving vapours |
|--|---|---|--|
| Uric | Blackened—
rapidly—
Tartaric
Tannic
Gallic

slowly—
Citric
Evolving smell of vinegar

Acetic
Evolving aromatic and irritat-
ing vapours

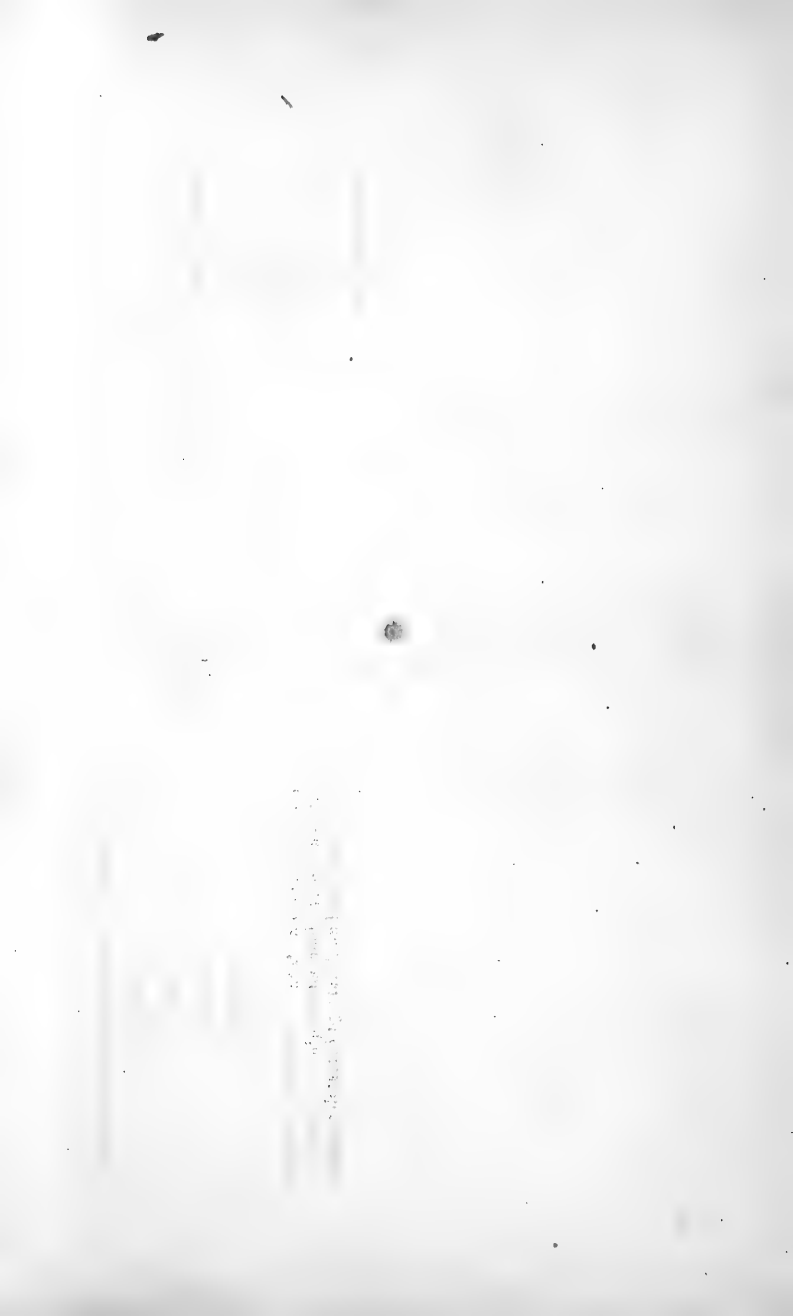
Benzoic
Evolving gas which burns
with blue flame

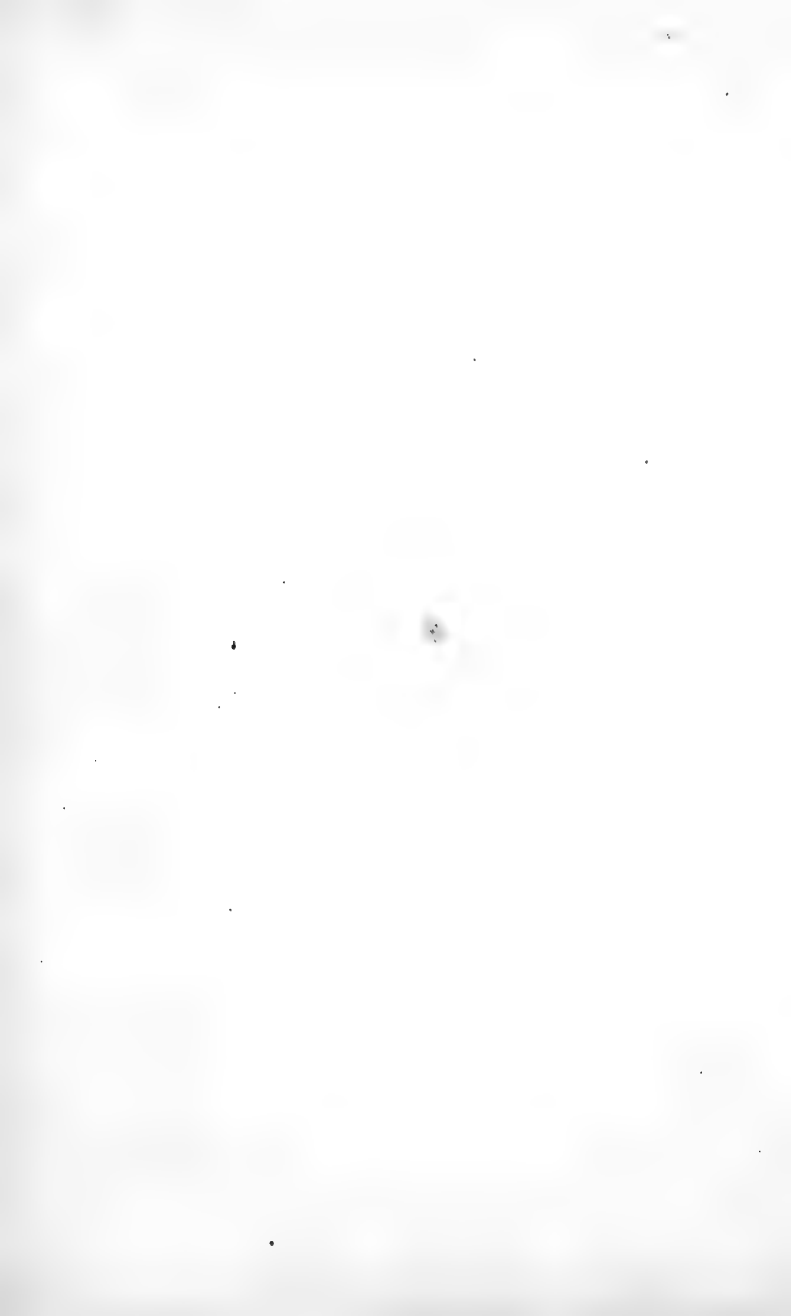
Oxalic | Giving a precipitate with solu-
tion of gelatine
Tannic

Giving no precipitate with solu-
tion of gelatine
Gallic | Smelling of burnt sugar
Tartaric

Smelling acid
Citric

Smelling aromatic
Benzoic |





1ST DIVISION OF GROUP II.

Evolving a gas on addition of dilute $H^2S O^4$

Odorous
Sulphurous
Inodorous
Carbonic

It may be necessary to heat in order to obtain the smell of sulphurous acid, which may be further detected by starch and iodic acid.

The barium precipitate treated with hydrochloric acid is

| | | | | | | | | | | | |
|------------|---|--------|-------|------------|---------|--|---------|--|--------------|--|--------|
| Insoluble | Soluble | | | | | | | | | | |
| Sulphuric | Precipitate with $Ag N O^3$ in original solution is | | | | | | | | | | |
| | <table border="0"> <tr> <td>Yellow</td> <td>White</td> </tr> <tr> <td>Phosphoric</td> <td>Boracic</td> </tr> <tr> <td></td> <td>Silicic</td> </tr> <tr> <td></td> <td>Hydrofluoric</td> </tr> <tr> <td></td> <td>Oxalic</td> </tr> </table> | Yellow | White | Phosphoric | Boracic | | Silicic | | Hydrofluoric | | Oxalic |
| Yellow | White | | | | | | | | | | |
| Phosphoric | Boracic | | | | | | | | | | |
| | Silicic | | | | | | | | | | |
| | Hydrofluoric | | | | | | | | | | |
| | Oxalic | | | | | | | | | | |
| | See special tests. | | | | | | | | | | |

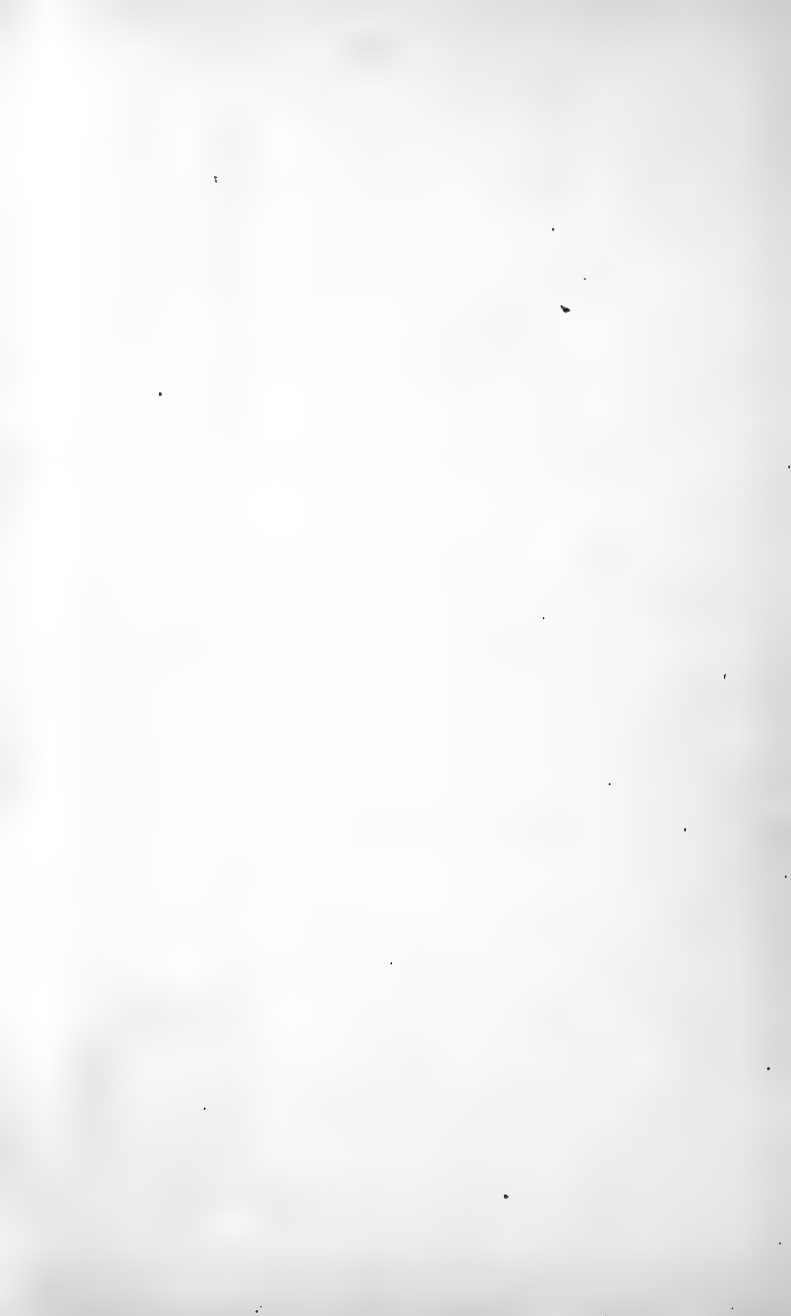
2ND DIVISION OF GROUP II.

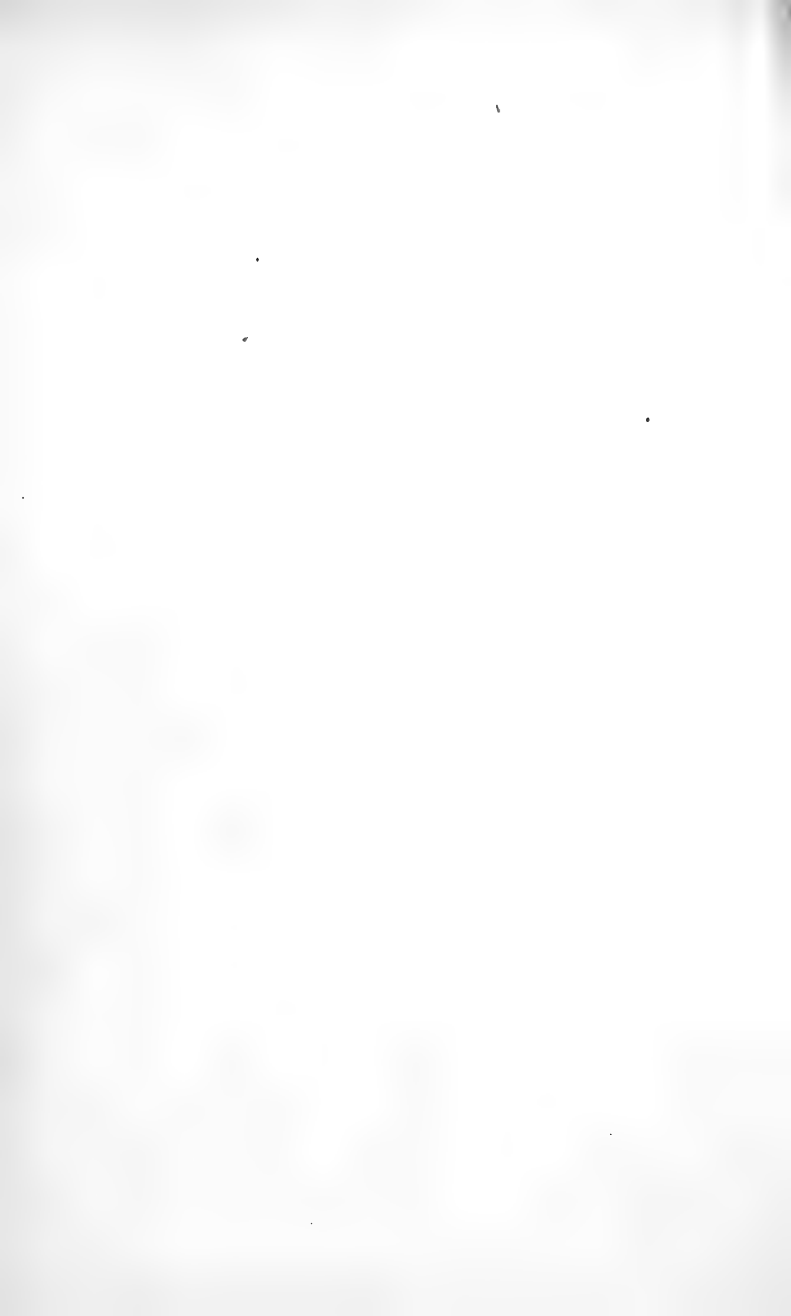
Precipitate with AgNO_3 is

| Black. | Yellowish red. | Yellowish. | White. |
|----------------|------------------|--------------------------|---|
| Hydrosulphuric | Hydroferrieyanic | Hydriodic
Hydrobromic | Hydrochloric
Hydroferroeyanic
Sulphocyanic
Hydroeyanic |

Ferric chloride gives

| Opalescence in acid or black precipitate in neutral solutions. | Brown colour. | No colour or precipitate. | No colour or precipitate. |
|--|------------------|---------------------------|--|
| Hydrosulphuric | Hydroferrieyanic | Hydriodic
Hydrobromic | Hydrochloric
Hydroeyanic |
| | | | Dark blue precipitate.
Hydroferroeyanic |
| | | | Red colour.
Sulphocyanic |





GROUP III.

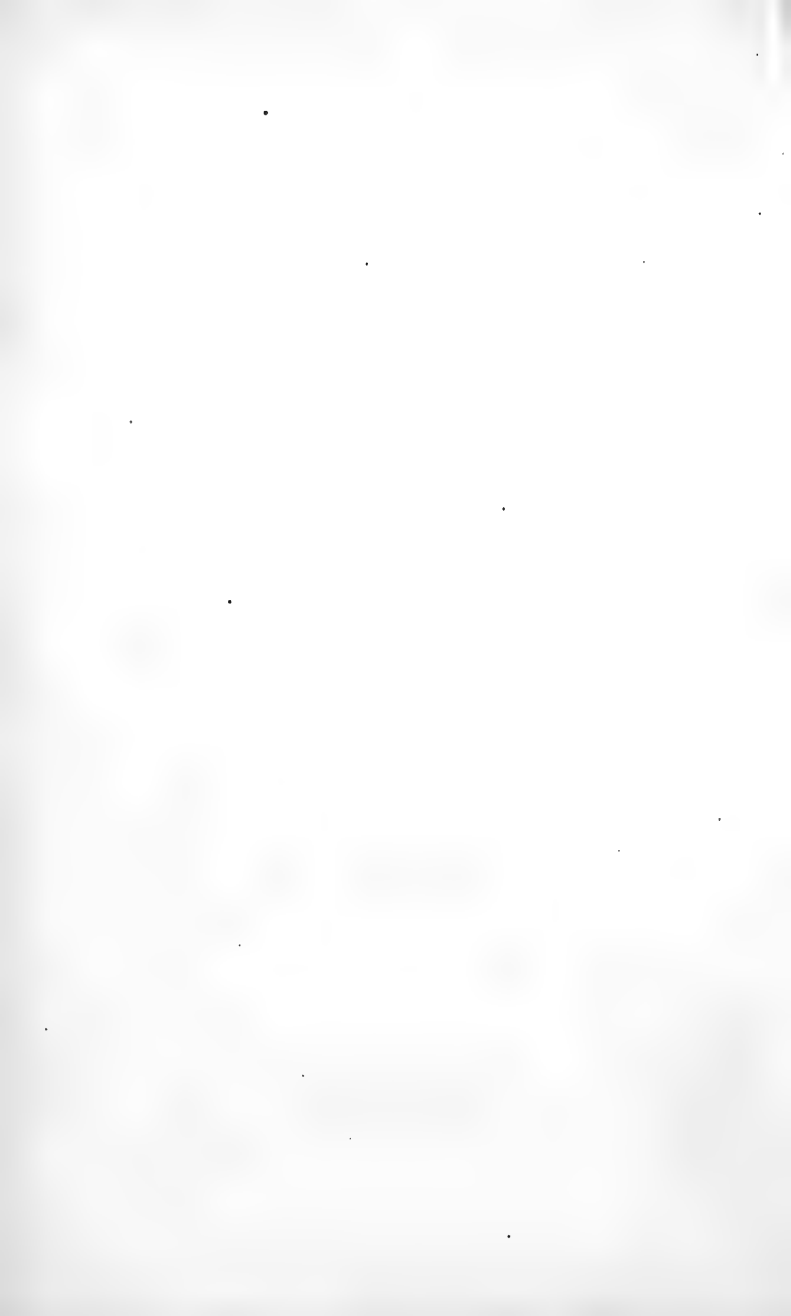
| Giving off violet fumes when heated on charcoal. | Giving red fumes when heated with Cu and H^2SO_4 | Giving yellow colour and explosive gas when heated with H^2SO_4 |
|---|--|---|
| <p>Iodic</p> <p>Iodates give a precipitate with barium chloride.</p> | <p>Nitric</p> | <p>Chloric</p> <p>Salts give no precipitate with $AgNO_3$ until strongly heated and re-dissolved.</p> |

TABLE II.

| Precipitated from neutral
* solutions by BaCl ₂ | Precipitated from neutral
solutions by CaCl ₂ | Precipitated from neutral
solutions by AgNO ₃ | Neutral solutions mixed
with Fe ³ Cl ₃ give | Salts decomposed on
charcoal |
|--|--|---|--|---|
| Precipitate insoluble in HCl
Sulphuric
Soluble in HCl
Carbonic
Phosphoric
Boracic
Oxalic
Hydrofluoric
Tartaric
Citric
Chromic
Arsenious
Arsenic | Precipitated at once.
Insoluble in acetic acid.
Oxalic
Hydrofluoric
Soluble in acetic acid.
Carbonic
Phosphoric
Boracic
Tartaric
Arsenious
Arsenic
Precipitated after boiling.
Citric | Insoluble in HNO ₃
White.
Hydrochloric
Hydrocyanic
Hydroferrocyanic
Sulphocyanic
Yellowish.
Hydrobromic
Hydriodic
Hydroferrocyanic
Soluble in HNO ₃
White.
Carbonic
Boracic
Oxalic
Tartaric
Citric
Yellow.
Phosphoric
Arsenious
Red brown.
Chromic
Arsenic
Black.
Hydrosulphuric | A white precipitate.
Phosphoric
A blue precipitate.
Hydroferrocyanic
A brown colour.
Hydroferrocyanic
A red colour.
Acetic
Sulphocyanic | Chloric
Iodic
Nitric |

* The solutions must be perfectly neutral, obtained by adding N K₃ and boiling until the smell of NH₃ is no longer perceptible. The solutions used in column 3 must not be very concentrated, as acetates will give a precipitate with AgNO₃ if not diluted.





SUBSTANCES INSOLUBLE IN WATER.

In the preceding pages those substances only have been considered which are soluble in water, except when as in the cases of bismuth salts, &c., decomposition ensues. The examination of bodies insoluble in water is somewhat more difficult, the substance should be treated successively with water, hydrochloric acid, nitric acid and a mixture of the last two, and the solution obtained in each case evaporated to see if any thing has been dissolved. In using the mixture of the two last named acids, the solution must not be evaporated in a platinum capsule, as that metal would be dissolved. In each case the liquid being poured off and the residue washed repeatedly with water, any insoluble matter that remains may be treated with the re-agents above mentioned.

A The substance exhibits a metallic lustre or glance, especially on recent fractures.

B The substance appears to be of an earthy character.

A

1. The substance treated with hydrochloric acid dissolves readily with evolution of hydrogen. Magnesium, aluminum, and metals of the iron class, and also tin and cadmium. The solutions may be examined by the proper tests for these metals.

2. The substance treated with nitric acid dissolves readily with evolution of red fumes and without the formation of sulphuric acid; copper, bismuth, mercury, &c.

3. The substance is converted by nitric acid into a white powder; tin and antimony.

4. The substance is not acted on by either hydrochloric or nitric acid, but is dissolved by a mixture of the two: gold, platinum.

5. The substance is dissolved by hydrochloric acid under evolution of hydrosulphuric acid; ferrous, antimonious or bismuth sulphide. Some other sulphides such as those of zinc and manganese would be acted on in a similar manner.

6. The substance is acted on by nitric acid with evolution of red fumes, and the solution obtained is found to contain sulphuric acid. The solution must be very much diluted before applying the barium nitrate for the detection of the above-named acid. Almost all metallic sulphides. Of natural ores cinnabar may be mentioned as an exception.

7. The substance, by boiling with nitric acid, is converted into a white powder, soluble in strong hydrochloric acid; lead sulphide. In this case a portion of the metal will generally, unless very strong acid be used, remain in solution in the nitric acid; while in the case of tin and antimony no trace is dissolved. Stannic oxide (3) and antimonious oxide (3) may also be soluble in hydrochloric acid.

8. The metals will mostly melt before the blowpipe flame and form incrustations on the charcoal (see the several metals). Gold and platinum are infusible. Many sulphides will give off fumes of sulphurous acid, burning with a blue flame, and lead and bismuth sulphides will give easily a metallic bead.

9. The presence of copper in sulphides may be detected by roasting a particle in the blowpipe flame, moistening with hydrochloric acid and again exposing to the flame, a bluish colour will be seen if copper is present. The ore may also, when in fine powder, be digested in nitric acid, the solution supersaturated with ammonia, when a blue solution will indicate copper, a brownish red precipitate will show the presence of iron.

10. The addition of hydrochloric acid to the nitric solution and the production of a white precipitate soluble in ammonia will indicate silver, but when very small quantities of this metal are present recourse must be had to cupellation.

B.

The substance does not exhibit a metallic lustre or glance, and is insoluble or nearly so in hot hydrochloric acid.

The dry substance is treated with ammonium sulphide.

1. The first of the main results is

the following theorem

Let f be a function

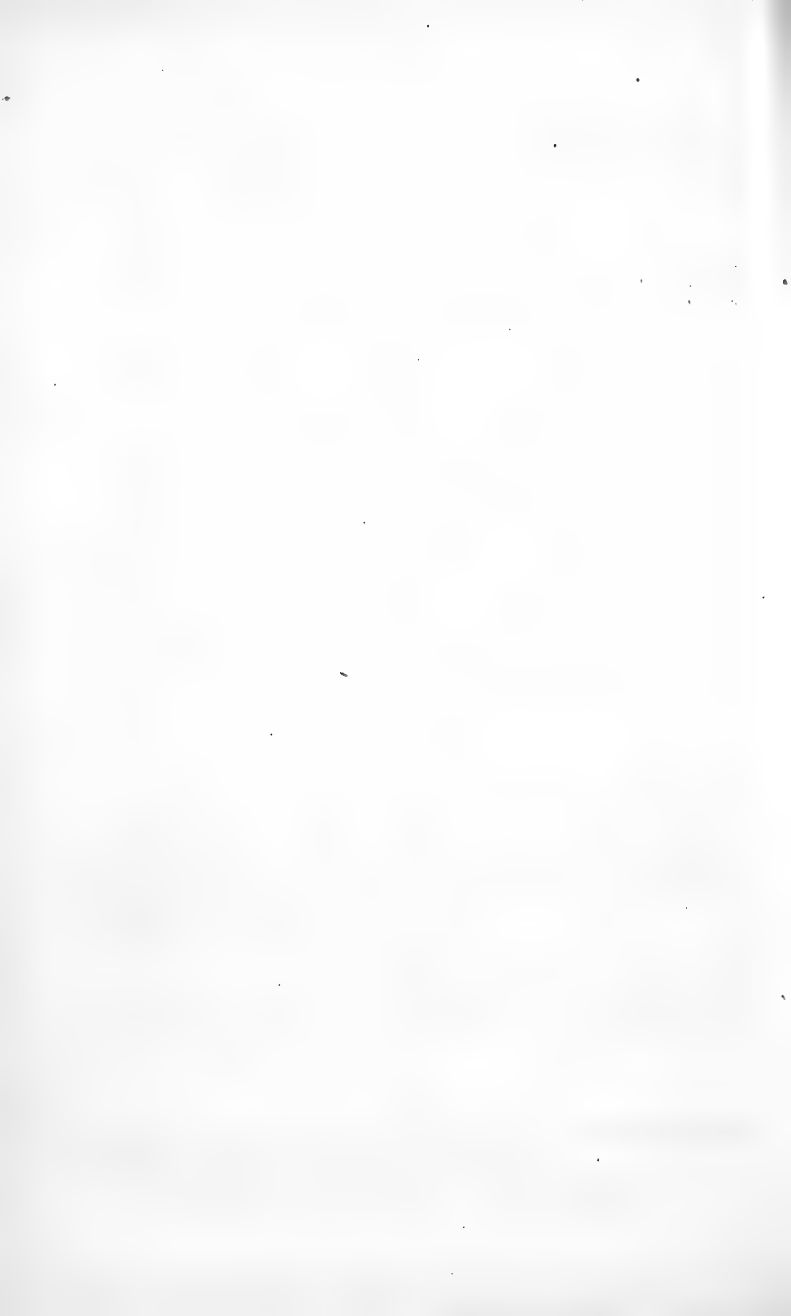
defined on the interval

and let F be its indefinite integral

then the function F is continuous on the interval $[a, b]$

and

the function F is continuous on the interval $[a, b]$
as has been proved with



TURNS BLACK.

Some salts of silver, lead, or mercury.

CALOMEL (Hg Cl) may be recognised at once by being blackened by N H^3 , by giving a sublimate of metallic mercury when heated with sodium carbonate, and by being dissolved by hot nitrohydrochloric acid, the solution giving the re-actions of mercuric oxide.

LEAD in the sulphate (iodide and chloride) may best be recognised by fusing with sodium carbonate on charcoal, when a malleable bead will be produced, which may be further examined. The acid may be detected by boiling or fusing (in a porcelain crucible) with sodium carbonate, and testing the solution obtained.*

SILVER may be detected in the same manner; the metallic bead obtained may be dissolved in nitric acid and the proper tests applied.

NOT CHANGED.

Sulphates of the alkaline earths, alumina and aluminates, silica and silicates.

The SULPHATES may be decomposed by fusing or long boiling with sodium carbonate, filtering and washing. In the filtrate the acid may be detected after supersaturation with pure nitric acid. The base may be detected in the residue remaining on the filter after dissolving it in dilute hydrochloric acid.†

ALUMINA in its insoluble form and aluminates are best recognised by fusing with sodium carbonate, dissolving the fused mass in hydrochloric acid, and precipitating with ammonia. If the precipitate is reddish, it may be digested with potassium hydrate which dissolves the alumina, and filtered. This solution can be precipitated by ammonium chloride, and the deposit tested for alumina. Silica and silicates (see next paragraph).

SILICA AND SILICATES.

Pure silicic acid may, when in fine powder, be dissolved by strong boiling solution of sodium carbonate, or by fusion with the same when a clear liquid is formed under effervescence, which can be dissolved in water. The solution in either case is decomposed by hydrochloric acid, either with separation of gelatinous silica at once, or as an insoluble powder after evaporation of the acid solution to dryness, and treatment with water.

Some silicates when in fine powder are decomposed by hydrochloric acid even in the cold, with separation of more or less gelatinous silica; the whole is evaporated to dryness, moistened again

* Lead sulphate is soluble in boiling hydrochloric acid, and the iodide and chloride in a large excess of boiling water.

† The sulphates of the earths may be readily decomposed by deflagrating with 2 parts fine charcoal and 12 parts potassium nitrate; on boiling with water and washing, the carbonates will remain undissolved.

with hydrochloric acid, filtered and the bases detected by appropriate tests in the filtrate; the residue is pure silica.

Others must be fused with sodium carbonate, or a mixture of equal parts of sodium and potassium carbonate; the fused mass treated with hydrochloric acid to strong acid re-action, evaporated to dryness and treated as above.

Some silicates resist even this method of decomposition. When they contain alkalies they must be decomposed by hydrofluoric acid, or by fusing with calcium carbonate (4 parts) and ammonium chloride (1 part).

If the alkalies have to be detected the fused mass may be boiled with water which dissolves out the alkalic chlorides. The latter process is preferable to that with hydrofluoric acid. It is scarcely necessary to mention that a platinum crucible must be used for such experiments. The crucible should be imbedded in magnesia contained in a hessian or common earthenware crucible, and heated strongly for at least half an hour.

ADDENDA.

CHROMIC IRON ORE.

This dark coloured mineral is scarcely acted on at all by acids, it may be recognised by fusing it in extremely fine powder with hydric-potassium sulphate (bisulphate of potassa). The fused mass is dissolved in water, filtered, precipitated by ammonia, rapidly filtered and washed, the precipitate dried and fused with nitre. The fused mass treated with water gives a yellow solution in which chromic acid may be detected. The chromic oxide may also be detected by the appropriate blowpipe test.

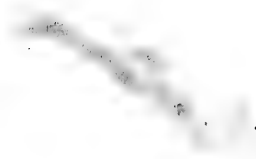
For other methods of decomposing chromic iron ore see Fresenius.

TITANIC IRON ORE.

This rather common Canadian mineral is often mistaken for magnetic iron ore, it occurs in large quantities in the neighbourhood of Gananoque.

It is also found in some of our Canadian black sands. It may be recognised by its insolubility in hydrochloric acid, and is best detected by fusion, in very fine powder, with hydric potassium sulphate. The fused mass is digested with a large quantity of water,

... and ...
...
...
...
...



and the solution boiled for some time, when from the colourless solution a precipitate of titanio acid is formed, generally of a yellowish or brownish colour from the presence of ferric oxide. Boiling nitric acid will sometimes extract the ferric oxide from this precipitate and leave pure white titanio acid.

WOLFRAM.

A compound of tungstic acid or oxide with ferric or ferrous oxide. The mineral is of a dark colour, when finely powdered and digested for a long time with hydrochloric acid, a yellow powder is produced which dissolves in ammonia or potassium hydrate. The solution gives with nitric acid a white precipitate, which on boiling with excess of acid becomes yellow. The precipitate is insoluble in acids, herein differing from molybdic acid. A tungstate heated with stannous chloride and a little hydrochloric acid gives rise to a fine blue colour. For further tests see Fresenius.

MOLYBDENITE.

MOLYBDENUM SULPHIDE.

This mineral which greatly resembles plumbago is found in considerable quantities about Lake Superior. The ore may be ground fine and roasted for a considerable time at a low red heat. Yellow molybdic acid is formed which can be dissolved out by ammonia, the solution when mixed with nitric acid gives a white precipitate soluble in excess. Hydrochloric acid acts in the same way, and if zinc or tin be placed in this solution it becomes blue, green and finally black. For further tests see Fresenius.

PITCHBLEND.

This mineral which is of a pitchy black colour is found in some parts of Canada. For detecting the uranium contained in it, the mineral should be finely pulverised, digested in nitric acid until all action ceases even on addition of more acid, the solution diluted with water and treated with hydrosulphuric acid until no more precipitate is formed; the filtrate from the precipitate may be evaporated to dryness and the residue treated with ether, which on evaporation will yield the yellow uranium nitrate.

Salts of uranium give a yellow precipitate with potassium hydrate, a red brown precipitate with potassium ferrocyanide and none with hydrosulphuric acid in acid solutions.

COMPLEX MIXTURE.

It is not within the scope of this work to give methods for the analysis of all possible mixtures; the reader is referred to "Fresenius' Qualitative Analysis," or other large works. A few examples only of more commonly occurring mixtures will be given, and the student is reminded that by the use of the tables for the bases and acids they may be divided into groups. The table for the grouping of bases leaves nothing to be desired, but for the acids the arrangement is not so perfect.

In examining for bases, if hydrochloric acid be added in slight excess and the precipitate separated by filtration, no metals of the first group can be present in the filtrate except a trace of lead. If excess of hydrosulphuric acid be added to this filtrate and the precipitate filtered off, no metals of the second group can be contained in the filtrate, and so on; bearing in mind that for detecting the metals of the last group the original salt or solution must be used.

GROUP I.

SILVER. LEAD. MERCURY (AS MERCUROUS SALT).

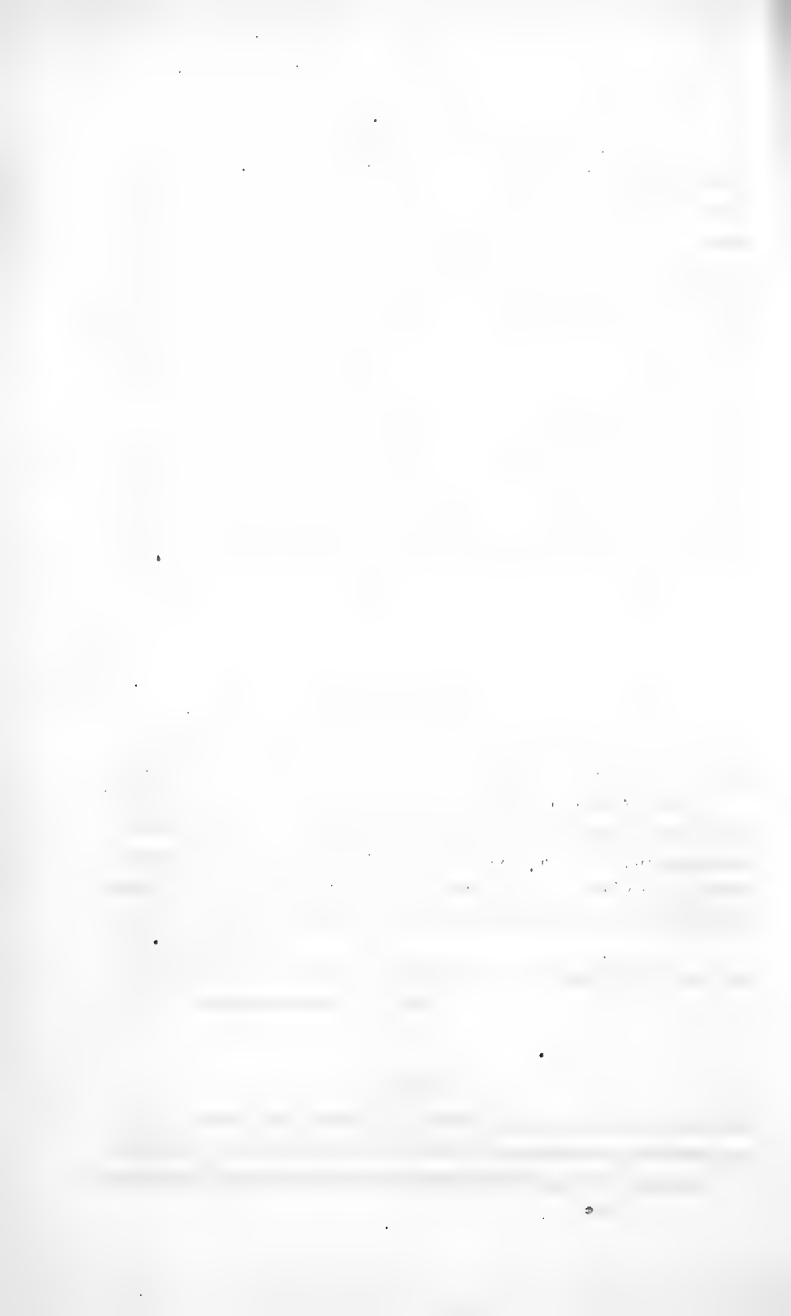
The precipitated chlorides may be boiled with water as long as anything is dissolved, and the lead detected in the solution by hydrosulphuric acid, sulphuric acid or other appropriate tests.

The residue may be treated with ammonia which will dissolve the silver chloride and leave a black residue of mercurous chloramide. The solution will give a precipitate on addition of nitric acid, and from this metallic silver may be obtained by fusing with sodium carbonate.

The black residue may be examined for mercury by heating in a small tube with sodium carbonate.

GROUP II.

If the precipitate formed by hydrosulphuric acid is yellow or orange all those metals which form dark coloured sulphides are excluded, if the precipitate is dark coloured all may be present.



The washed precipitate is digested with excess of ammonium sulphide and filtered.

No residue is left—absence of metals of division B.

FIRST DIVISION, A.

The solution of the sulphides in ammonium sulphide is treated with hydrochloric acid. A precipitate which, after drying, does not burn away completely on the application of a moderate heat, indicates gold, platinum, tin, or antimony. As the first two metals are very rare, and occurring in a metallic state are easily recognisable, we may confine ourselves to tin, antimony and arsenic.

The mixed sulphides are fused with sodium nitrate and a little carbonate, the fused mass treated with water yields up arsenic acid recognisable by proper tests; the residue consists of stannic and antimonious oxides which may be fused with potassium cyanide. The resulting bead of metal, when pulverised and boiled with hydrochloric acid, yields a solution of stannous chloride recognisable by proper tests (see page 39), and the residue, if any, may be tested for antimony by the action of the blowpipe, nitric acid, &c., &c.

SECOND DIVISION, B.

A yellow residue is left—absence of all metals in division B except cadmium. This yellow substance may be tested for cadmium.

A dark coloured residue is left—possible presence of all metals included in division B.

The residue is digested after washing, with dilute sulphuric acid which will dissolve out the cadmium, precipitable again from the solution by hydrosulphuric acid. The washed residue when treated with nitric acid will dissolve entirely if mercuric sulphide is absent, if a black residue remains it must be dissolved in nitrohydrochloric acid and the solution tested for mercuric oxide. The solution in nitric acid should be evaporated to dryness and treated with water, an insoluble residue indicates bismuth which may be further recognised by appropriate tests, the filtered solution will give a blue colour with ammonia if copper is present, and a white precipitate with sulphuric acid if lead is contained in the solution. When very strong nitric acid is used the lead sulphide is entirely converted into sulphate and remains undissolved. It may be extracted

by boiling with strong hydrochloric acid or solution of ammonium tartrate or acetate.

GROUP III.

IRON. COBALT. NICKEL. MANGANESE. CHROMIUM. ZINC.
ALUMINUM.

It is not likely that all these metals should occur together, but to detect them the precipitate may be examined as to its colour, if not black it cannot contain any of the first three. If black it may contain them all. If white or nearly white it cannot contain any but the last two.

Supposing that the precipitate is black and may therefore contain all the above metals, dilute hydrochloric should be added to the *well washed* precipitate—if a black residue remains it must consist of nickel or cobalt sulphide or both. For the separation of these use the cyanide test.

Iron and aluminum may be separated by boiling the nearly neutralised solution with excess of sodium acetate, the precipitate consists of ferric oxide and alumina, the latter easily extracted by potassium hydrate and precipitated by ammonium chloride. Sodium carbonate will precipitate the other metals from the filtrate. In this precipitate the manganese may be detected by fusion with sodium carbonate, the chromium by fusion with potassium nitrate, washing with water and testing the yellow liquid for chromic acid, and the zinc by fusion of the residue with a reducing agent on charcoal, when an incrustation will be formed, yellow when hot but white when cold.

GROUP IV.

BARIUM. STRONTIUM. CALCIUM. MAGNESIUM.

The first three may be separated from the fourth by dissolving the precipitate of mixed carbonates in dilute hydrochloric acid, adding excess of ammonium chloride and then ammonium carbonate, the magnesium will remain in solution and may be detected by sodium phosphate. The separated precipitate may be dissolved in hydrochloric acid and evaporated to dryness to drive off excess

1. Statement of the Bureau and the
Office of Very Large Enterprises

2. Statement of the Bureau and the
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3. Statement of the Bureau and the
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4. Statement of the Bureau and the
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5. Statement of the Bureau and the
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of acid. Potassium chromate added to the solution of this residue will precipitate all the barium, and the strontium may be detected in the filtrate by very dilute sulphuric acid or calcium sulphate. Another portion of the solution of the residue may be precipitated by potassium sulphate, allowed to stand some hours, filtered, and the filtrate tested for calcium by ammonium oxalate. Of course only a small quantity of calcium will be found in this solution owing to the difficult solubility of the sulphate.

GROUP V.

POTASSIUM. SODIUM. AMMONIUM.

The evolution of ammonia on heating a portion of the dry substance with potassium hydrate shows the presence of ammonium. The remainder is then heated until no more fumes are given off, moistened with water and burnt with alcohol. A yellow colour indicates sodium; the residue is dissolved in a small quantity of water and tested for potassium by platinic chloride or tartaric acid.

COMPLEX MIXTURES OF ACIDS.

The detection of acids when several occur together or when they exist in insoluble substances, is much more difficult than that of the bases. If combined with an oxide of a heavy metal, the action of hydrosulphuric acid may be employed to separate the acid, either on the solid body or on its solution in some acid; digestion with ammonium sulphide may also be resorted to, or the substance may be boiled with sodium carbonate for some time. In the latter case the solution should be acidulated with pure nitric acid, supersaturated with ammonia and boiled till perfectly neutral to test paper. In all cases of testing for acids the above neutralisation should be carefully observed. It is seldom that many acids occur together unless in samples given for practice, and the chemist has to rely principally upon special tests.

ORGANIC ACIDS GIVING WHEN IN NEUTRAL SOLUTION A PRECIPITATE WITH BARIUM CHLORIDE.

Gallic and tannic acid may be detected by their action on salts of iron, and separated from each other by a solution of gelatine which precipitates the latter. Benzoic acid by being precipitated from solutions by an acid and by special tests applied to the precipitated crystals.

Uric acid by the action of nitric acid and of potassium hydrate.

Tartaric and citric by giving precipitates with perfectly neutral calcium chloride, the former in the cold, the latter after boiling, separation of the two may in this way be effected.

Acetic acid does not give a precipitate with barium on calcium chloride, but may be referred to here as being an organic acid. It may be detected by giving a red colour with ferric chloride and by yielding sweet smelling ethyl acetate when distilled with alcohol and sulphuric acid.

INORGANIC ACIDS GIVING A PRECIPITATE WITH BARIUM CHLORIDE.

Sulphuric acid may at once be separated from a mixture by the insolubility of the precipitated sulphate in hydrochloric acid, the

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solution may be neutralised with ammonia and the precipitate decomposed by sodium carbonate as above described.

If the precipitate dissolves with effervescence carbonic acid may be present, and sulphurous acid may be detected by heating the salt with moderately strong sulphuric acid and allowing the vapours evolved to act on starch and iodic acid.

A neutral solution having again been obtained it may be treated with calcium chloride and the precipitate digested with acetic acid, fluoride and oxalate will remain undissolved and may be recognised by appropriate tests, the solution may also be tested specially for phosphoric and boracic acid, &c.

ACIDS NOT GIVING A PRECIPITATE WITH SOMEWHAT DILUTE SOLUTIONS OF BARIUM CHLORIDE, BUT WITH SILVER NITRATE.

† Great difficulty would occur in separating the acids of this group if many occurred together, but students are not likely to meet with very complicated mixtures.

Hydrosulphuric acid may always be recognised by its action on salts of lead, and may be expelled by boiling with acid.

Hydrochloric acid by the pungent vapours evolved when its salts are treated with strong sulphuric acid, and by giving a white precipitate with silver nitrate easily soluble in ammonia, which is fused into a horny mass by strong heat.

Hydrocyanic acid by evolving a well known smell when treated as above. If masked by the preceding acid it may be detected by forming the silver precipitate, which is easily soluble in ammonia. This solution may be again precipitated by the addition of nitric acid, the precipitate dried and heated, when cyanogen will be evolved (burning with a violet coloured flame), and the residue will contain metallic silver, which can be extracted by nitric acid, and its presence detected; the bromide and chloride are not decomposed by heat. The silver precipitates, insoluble or nearly so in weak ammonia, may contain bromide and iodide. By digesting with strong ammonia at a moderate heat all the bromide may be dissolved and the iodide left. The bromide may be reprecipitated by nitric acid, and it as well as the iodide decomposed by zinc and sulphuric acid, or better by sodium amalgam, and the resulting solutions examined.

POISONS.

Almost all substances when used in improper quantities may act as poisons, thus nitre and acetic acid have been known to produce injurious results. In the following pages, only those substances will be considered which when administered in moderate amounts may produce fatal effects either by their physical or physiological action.

SULPHURIC ACID.

The free acid may be detected by the tests described at page 46 ; if mixed with organic matter, as in the contents of the stomach, a clear solution should be obtained and the appropriate tests applied, bearing in mind that traces of sulphate will always be found ; but the strongly acid character of the mixture will indicate free acid. If lime or chalk has been administered as an antidote, the insoluble matter must be examined as described at page 46. If the acid has been thrown upon parts of the clothing, these may be boiled in water and the proper tests applied to the filtered solution.

NITRIC ACID.

Is seldom used as a poison, but accidents may occur from its use. By neutralising with potassium carbonate and evaporating the solution crystals of nitre may be obtained, which can be recognised by the proper tests, see page 54.

OXALIC ACID.

This substance has sometimes been used by mistake instead of magnesium sulphate (Epsom salts), from which it may be readily distinguished by the striated and somewhat opaque crystals, its strongly acid taste, and its entire volatility when heated on platinum foil. Other tests will be found at page 44.

Acid oxalates are sometimes sold under the name of salt of lemon ; easily distinguished from citric acid by blackening but slightly when heated, giving off no very acid vapours, and leaving a residue which effervesces strongly with acids.

When mixed with organic matter, the whole must be digested with water, filtered, precipitated with lead acetate, the lead oxalate

collected, washed, decomposed by hydrosulphuric acid, filtered, and the filtrate tested for oxalic acid. The separation of the lead sulphide is often attended with difficulty; sulphuric acid may be substituted for the hydrosulphuric.

Sorrel and some other vegetable substances contain oxalates; the non-employment of them as food must be proved when only small quantities of oxalic acid have been detected.

If lime or magnesia has been administered as an antidote, the insoluble matter must be examined as described at page 68.

ARSENIC.

The chemist may be called on to detect this substance in a solution, such as Donovan's or Fowler's or in a solution of an arsenate; in a solid as in arsenic and arsenious acids, arsenates and arsenites, fly powder (metallic arsenic), sulphides and arsenides. It may also occur mixed with organic matter, as in food, the contents of the stomach, vomited matter, fæces, urine, or in the liver or other organs of the body.

If a solution has to be examined, the ordinary tests for arsenic may be employed; if it be Donovan's solution, hydrosulphuric acid will produce a black precipitate from which ammonia or ammonium sulphide will extract the arsenious sulphide. The solution on evaporation will leave the arsenical compound, which may then be examined by any of the tests previously described.

If a solid has to be examined, it may be heated by itself in a reduction tube when a white crystalline sublimate will be formed if it be arsenious acid, the octohedral form of the crystals is very characteristic and can be readily observed by aid of a pocket lens. A metallic sublimate will be formed, mixed probably with more or less of white crystalline arsenious acid, if the substance be metallic arsenic or arsenical pyrites. The ring formed may be tested as described at page 41.

The solid may be an arsenite such as Scheele's or Schweinfurth green, or it may be arsenious acid mixed with ferric oxide or other substances. In that case it should be heated in a reduction tube with sodium carbonate and potassium cyanide (or charcoal) when a metallic ring will be formed. Insoluble arsenites and arsenates may also be dissolved in acid and decomposed by hydrosulphuric acid,

the precipitated sulphide being recognised by its solubility in ammonia and by the test mentioned below.

It may be a sulphide such as orpiment when the same mixture of carbonate and cyanide may be employed, but it will generally be better to boil the sulphide repeatedly with nitric acid, to evaporate to dryness and to test the residue with the above mixture of carbonate and cyanide.

If the urine is suspected to contain arsenic, its presence may be proved by passing hydrosulphuric acid through the acidulated liquid, collecting the precipitate, filtering, drying and testing by any of the previously described methods.

The precipitated sulphide may readily be converted into arsenious acid by dissolving it in potassium hydrate and boiling with bismuthic hydrate, when bismuthic sulphide and potassium arsenite are formed. In this filtered solution the arsenious acid may be readily detected. If arsenic sulphide has been acted on, the solution will contain arsenic and not arsenious acid.

Contents of the stomach. If the presence of arsenic is suspected, the contents should be mixed with water and well stirred in a beaker glass, allowed to settle for a few moments, the liquid poured off and the operation repeated several times with fresh portions of water so as to remove organic matters as far as possible.

If a white crystalline and sandy residue remains, a portion of it should be dried and tested for arsenious acid by the dry tests or if in sufficient quantity by the liquid tests for that substance. A white crystalline sublimate when heated in a tube is very characteristic of arsenious acid.

If a black sandy residue remains, a portion may be heated in a tube when, if it be arsenic (fly powder), a brown or metallic ring will be formed to which the usual tests may be applied. Another portion may be heated with nitric acid, the solution evaporated to dryness and tested with silver nitrate when a brick red colour will indicate arsenic.

If no crystalline or black sediment is observed the whole of the contents and washings should be evaporated over a water bath until reduced to a thick mass and treated as hereafter described.

Stomach and other viscera. If no solid arsenic, either in the form of metal or arsenious acid has been found, it will be necessary



to test for the poison in various parts of the body. The stomach and the evaporated contents and washings should be examined separately, and also the liver, kidneys and spleen, as the detection of arsenic in the liver, &c., is of especial importance, as showing that the poison had been administered during life. If the liver after death had been exposed to a solution of arsenious acid, more will be found in the outer portions than in the inner, but such cases seldom occur, only after long interment in a soil which has been proved to contain arsenic. The whole of the intestines should be examined.

The solid parts should be cut up into small pieces and these or the evaporated contents or urine mixed with about an equal weight of hydrochloric acid of about the specific gravity of 1.11. This is readily obtained by mixing strong acid with an equal bulk of water. The purity of the acid must have been previously ascertained, if not free from arsenic, hydrosulphuric acid must be passed through it for several hours, the precipitate filtered off from the dilute acid, and the filtrate gently warmed till the smell of hydrosulphuric acid is lost.

The operation of dissolving and destroying the organic matter is now conducted as follows :

1. The mixture contained in a perfectly clean porcelain dish is heated over a water bath (a common saucepan may be used) and powdered potassium chlorate added from time to time as soon as the effervescence caused by the previous addition has ceased. The stomach, intestines and contents will be very readily dissolved, but the liver and kidneys require long digestion.

It has been recommended to conduct the operation in a retort connected with a receiver, to avoid loss of arsenic as chloride, but this renders the operation much more troublesome, and if the temperature of the mass be kept below 100° , no volatilisation of arsenious chloride need be feared. Of course the operation must be conducted under a chimney to carry off the fumes arising; as soon as all solid particles are disintegrated and nothing but a yellow flocculent matter remains in the liquid, an equal bulk of water is added and the heating continued till no smell of chlorine is observable. It may be necessary to add more hydrochloric acid if solid matter remains and no effervescence ensues on the addition of a fresh portion of chlorate.

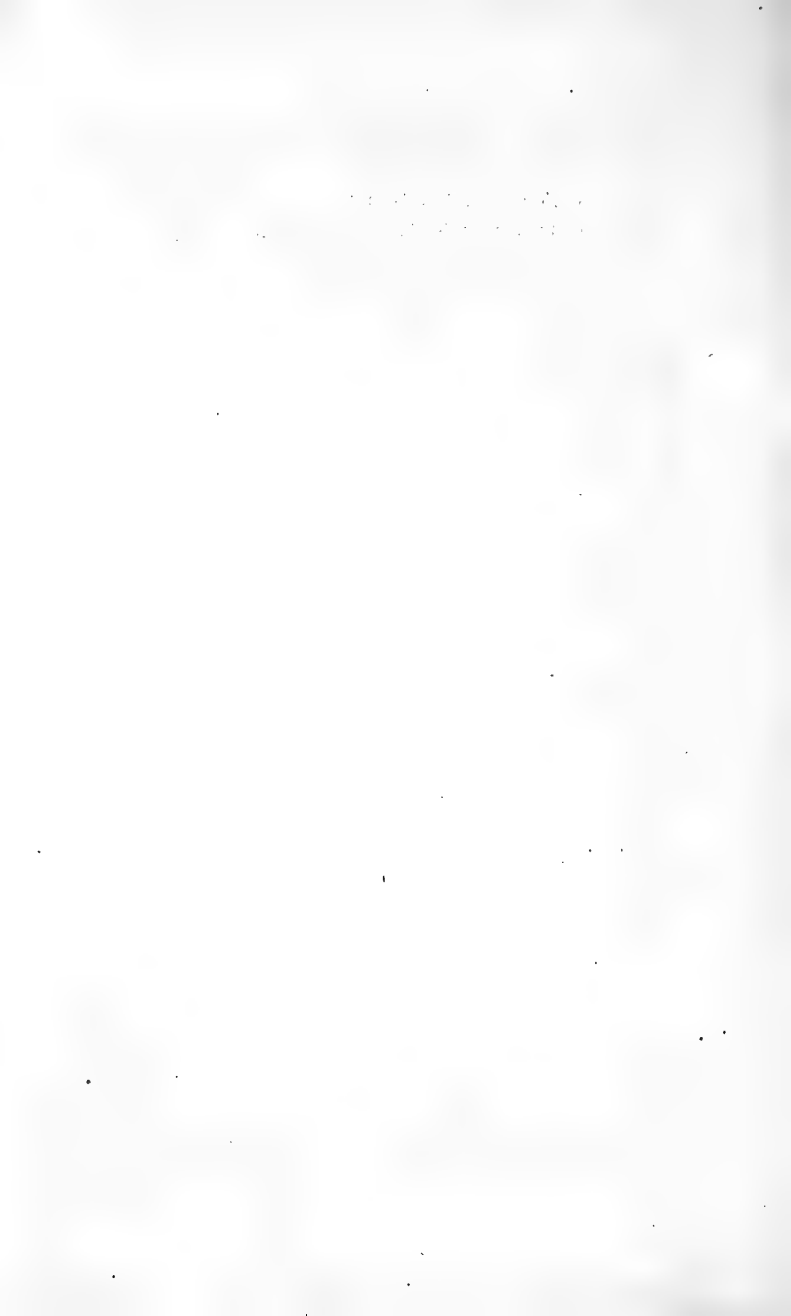
2. The whole must then be filtered through white filtering paper which should have been previously tested for arsenic as some specimens have been found to contain it; the residue well washed out with warm water and the filtrate, if too great in bulk, may be evaporated down to about a pint.

3. Washed hydrosulphuric acid is now passed in a moderate stream through the still hot solution, the precipitate formed thrown into a filter and well washed. The filtrate may deposit some more sulphide on standing or on evaporation. A pure yellow precipitate will indicate arsenic, an orange yellow antimony, and a brown or black mercury, lead, bismuth, &c. In these cases, however, arsenic may of course be present. A light coloured precipitate will often be formed even when no arsenic is present, from the action of a small quantity of chlorine still remaining in the solution. Such precipitate should be examined as if it were arsenious sulphide, that is by the following tests.

4. The precipitate while on the filter is drenched with ammonia by which the whole of the arsenic sulphide will be dissolved with only a trace of antimonious sulphide, the others will remain undissolved. The filtrate is evaporated to dryness in a clean porcelain dish in a water bath. The solution of the sulphide in ammonia may be aided by rubbing down with a feather.

5. The residue left after evaporation, which is generally of a brownish colour, is digested with fuming nitric acid; by long continued heating all the sulphur at first separated may be dissolved, but this is not absolutely necessary. The solution is neutralised with *pure* sodium carbonate and evaporated to perfect dryness. The carbonate must be free from chloride, the presence of sulphate is immaterial. By this process we have the arsenic converted into arsenic acid combined with soda, but organic matter may not be entirely absent; to remove this the next operation is adopted.

6. One or two drachms of pure sodium nitrate are fused in a porcelain crucible and the dry mass (5) thrown in gradually in small portions. A fresh portion should not be introduced until the blackening, which usually ensues, has entirely disappeared. By this process every trace of organic matter is destroyed and any free sulphur which may have been present converted into sulphuric acid. We have therefore in the fused mass sodium nitrate, sulphate and



arsenate, as by the fusion, if not by the previous action of nitric acid, all the arsenic will have been peroxidised. The nitric acid must now be got rid of.

7. Add pure sulphuric acid and heat until all red fumes cease to be evolved, and dense white vapours of sulphuric acid are formed. The operation should be conducted in a rather large crucible, and it may be necessary to add sulphuric acid from time to time.

A modification of the process will lead to the detection of antimony if any is present, viz., dissolving the fused mass in water when sodium antimonate will remain undissolved. The solution filtered off from the insoluble antimonate may be mixed with sulphuric acid, evaporated to dryness and treated as in the preceding paragraph. In this solution we have therefore arsenic and sulphuric acids with sodium sulphate.

8. The solution should be introduced into a burette or alkali-meter and the volume noted, a portion may then be tested by Marsh's apparatus.

A bottle with two necks, or a wide mouthed flask is fitted with a funnel reaching nearly to the bottom, and a delivery tube connected with a drying tube containing calcium chloride or potassium hydrate. This again is connected with a tube about 17 inches long, bent perpendicularly about 3 inches from the end and drawn out into a rather fine point or jet. In lack of a long stemmed funnel, a wide tube may be inserted into the cork and a small funnel placed in this.

Pure zinc and pure sulphuric acid diluted with 5 or 6 volumes of water are introduced into the bottle and the hydrogen allowed to pass off for a time, a portion of the tube near to the drying apparatus is then heated red hot by a spirit or gas-lamp, it may be prevented from bending by a covering of copper gauze, if no metallic ring is formed beyond the heated portion after a quarter of an hour, we may conclude that the materials used are free from arsenic. A small quantity of the solution (7) is then introduced while the tube is still heated, when a ring, more or less metallic, will be immediately produced if arsenic is present. The gas both before and after the addition of the suspected solution may be kindled at the drawn out point, and will burn with the well known pale flame if the hydrogen be pure, and with the characteristic bluish white colour if arsenic is present. If the stream of gas is slow all the arsenic

will be deposited in the tube, and only pure hydrogen will burn at the point, but if the stream is rapid, and the addition of arsenic causes the hydrogen to be evolved much more readily, a portion of the arseniuretted hydrogen may escape decomposition, and will give the above-named colour to the flame, which may be made to produce spots on porcelain plates held therein.

The bent portion of the tube may be turned round and introduced into a solution of silver nitrate. If arsenic is present, metallic silver will be precipitated, and all the arsenic remain in solution as silver arsenite, which may be precipitated by the careful addition of ammonia.

For delicate investigations the above apparatus is necessary, but for ordinary experiments a common 8 oz. phial may be used with a rather wide tube put through the cork, ground off obliquely below and drawn out into a not very fine point above. The hydrogen first evolved may be tested by its colour and by holding a porcelain plate or capsule in the flame about half way down. No spot will be produced if the materials are pure, but immediately after the introduction of the arsenical solution. Care should be taken not to hold the plate too long in the flame as the deposit of arsenic may be volatilised.

If the antimony has not been eliminated by the process described in 4 and 7 the spots or rings produced may be owing to the presence of that metal. To distinguish them from spots or rings produced by arsenic, the following experiments may be made.

The rings when gently heated volatilise completely—arsenic.

The rings when gently heated volatilise only partially, and on application of a strong heat leave metallic globules—antimony.

The ring when gently heated in a current of hydrosulphuric acid becomes yellow—arsenic.

The ring similarly treated becomes orange—antimony.

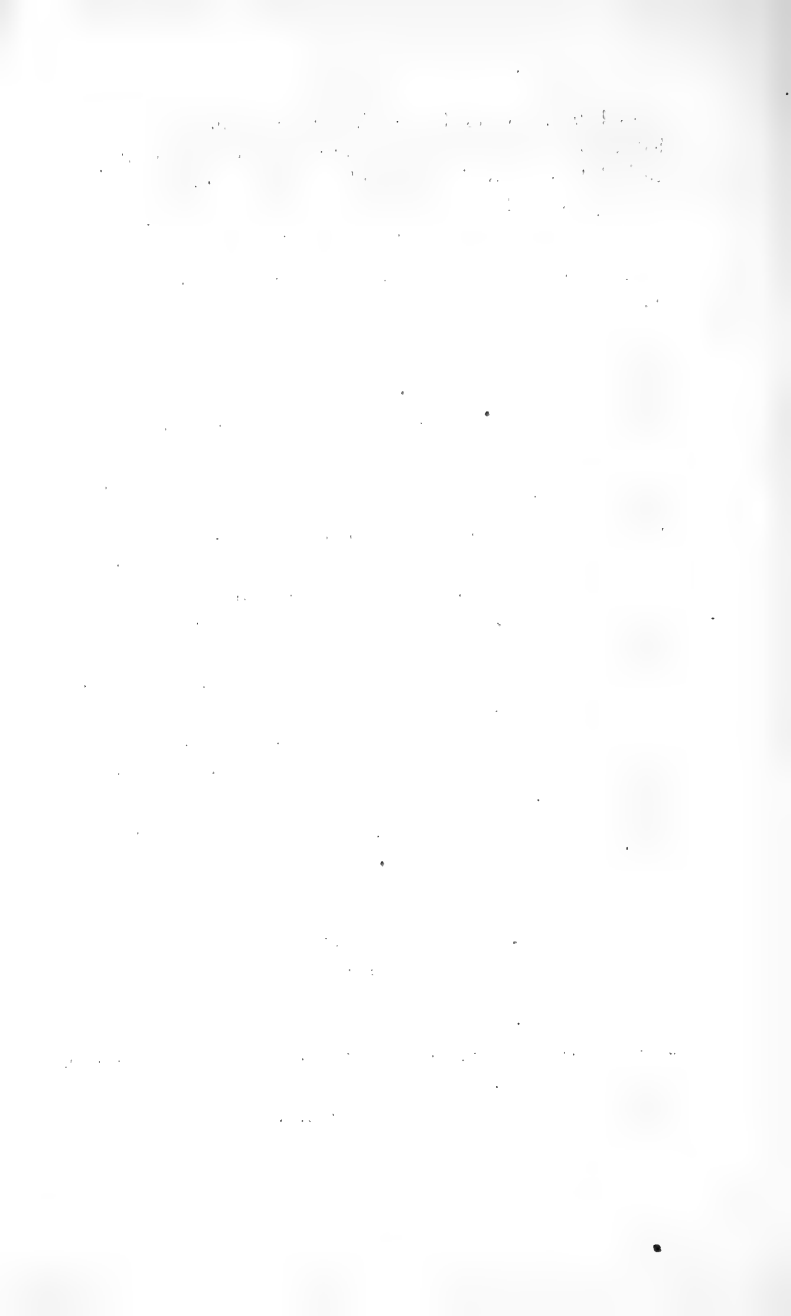
The coloured ring so produced, acted on by a current of hydrochloric acid, remains unchanged—arsenic.

Is dissolved and dissipated—antimony.

The ring or spot treated with a solution of potassium iodate dissolves with an evanescent reddish colour—arsenic.

The ring or spot is not dissolved by the same solution—antimony.

The ring or spot is dissolved by so-called chloride of soda—arsenic. It is not so dissolved—antimony.





The ring or spot treated with hot nitric acid and evaporated carefully to dryness until every trace of volatile acid is dissipated (the temperature must not be much above that of boiling water), gives with silver nitrate a brick red colour—arsenic. Similarly treated the ring or spot gives no colour—antimony.

The presence of arsenic having been proved by the above tests, it may be necessary to ascertain the quantity of the poison present, and it is desirable or advisable to do so in all cases requiring judicial investigation. The remainder of the liquid obtained in 7 may be treated in either of the following ways. It may be treated with sulphurous acid either in the form of gas or strong solution, boiled till all smell of sulphurous acid is lost, precipitated by a current of hydrosulphuric acid, the precipitate collected on a tared filter, washed, dried and weighed. Every 100 grains of the so-obtained arsenious sulphide correspond to or represent 80.4 of arsenious acid.

The solution obtained in 7 may also be mixed with a solution of magnesium sulphate and ammonia, allowed to stand for 24 hours, the precipitate of ammonio-magnesian arsenate filtered, washed with dilute ammonia, dried and weighed (the weight of the filter must have been previously ascertained), every 100 grains of the salt so obtained correspond to or represent 52.1 of arsenious acid.

From the quantity of sulphide or arsenate thus obtained from the portion of the solution remaining after detecting the arsenic, the whole quantity contained in the substance under examination may be easily calculated. The sulphide may also be dissolved in ammonia, the solution filtered, evaporated in a weighed capsule and the whole again weighed; by this process any precipitated sulphur is got rid of.

In testing for arsenic, it may be remarked (Wöhler), that the difficulty lies not so much in the detection of the poison as in the proof of its absence from the re-agents and materials employed. It is difficult to obtain zinc perfectly free from arsenic, many specimens of sulphuric acid contain the same impurity and will of course give arseniuretted hydrogen when used in Marsh's test. Even the filtering paper as before mentioned may occasionally contain arsenic.

PURIFICATION OF RE-AGENTS REQUIRED IN TESTING FOR ARSENIC.

Hydrochloric acid, the commercial article, may be diluted with an equal bulk of water and hydrosulphuric acid passed through it for several hours, filtered from the precipitate formed and gently warmed until no smell of hydrosulphuric acid is perceptible.

It may also be prepared by treating four parts of common salt with a cooled mixture of seven parts sulphuric acid with two of water, and conducting the gas evolved first through a small quantity of water contained in a two necked bottle, and thence into six ounces of water kept cool. The operation is continued as long as any gas is evolved, and the acid obtained will be sufficiently strong for the solution of organic matter as above described.

Sulphuric acid often contains arsenic and may be freed from it by diluting with twice its bulk of water and treating with hydrosulphuric acid, the excess may be expelled by heat after filtration.

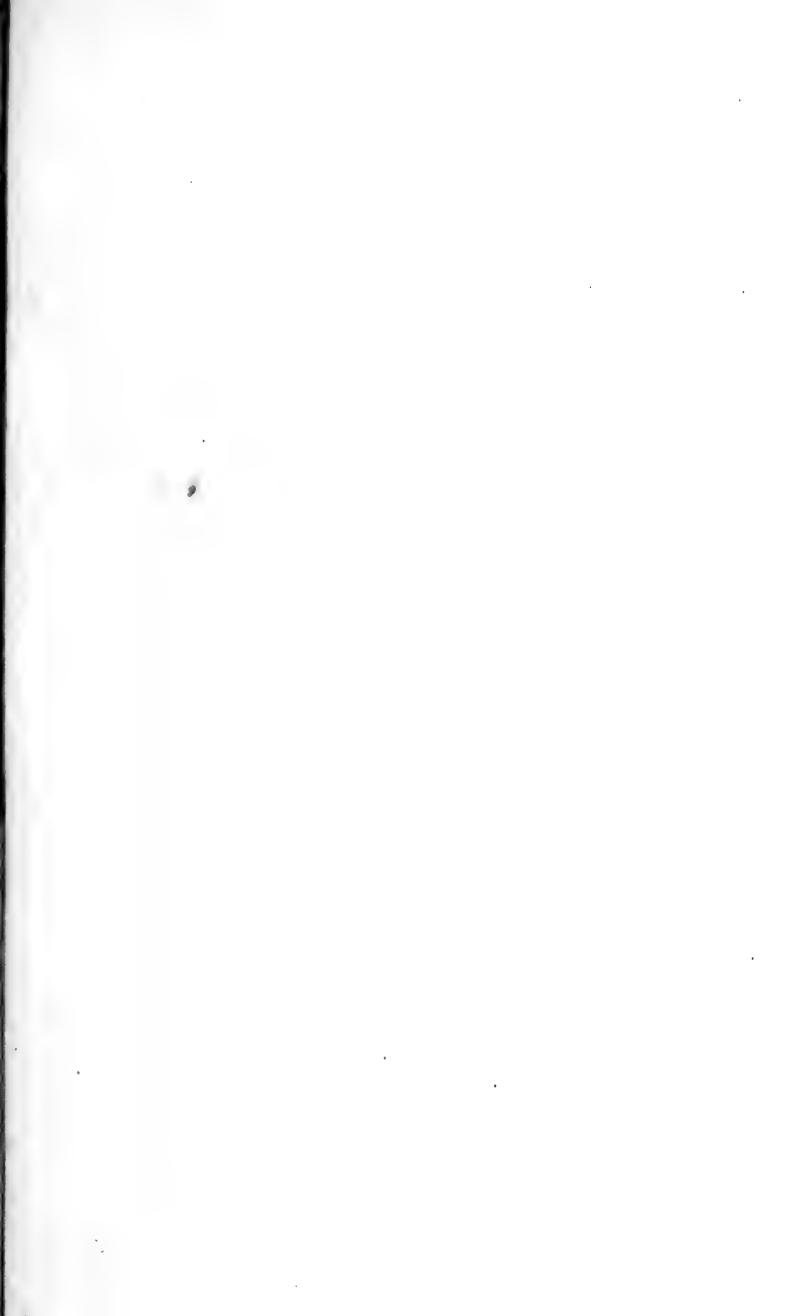
This acid may be concentrated by evaporation, but a pure strong acid may be obtained by heating strong sulphuric acid in a retort and passing hydrochloric acid gas into it for an hour or more; the distillate is tested from time to time with hydrosulphuric acid until it gives no yellow precipitate. The residue in the retort may also be tested by Marsh's apparatus, the greatest care being required to prove the absence of arsenic, and no reliance to be placed on the purity of commercial samples.

Carbonate of soda. This must be perfectly free from chloride, as otherwise in operation 7 the arsenic may be volatilised as chloride and lost. To obtain pure carbonate, the common so-called bicarbonate may be placed on a filter and washed with water until the washings give no precipitate, or even opalescence with silver nitrate after supersaturation with *pure* nitric acid.

Nitric acid must be free from hydrochloric, and may be obtained sufficiently pure by distilling as long as the distillate gives a precipitate or opalescence with silver nitrate. The residue may then be distilled over, or in most cases may be used at once as pure acid containing usually only small traces of impurity, which produces no injurious effect in the operations above described.

THE UNIVERSITY OF CHICAGO
DIVISION OF THE PHYSICAL SCIENCES
DEPARTMENT OF CHEMISTRY

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Zinc. The preparation of perfectly pure zinc can scarcely be effected unless in a well appointed laboratory, but commercial samples may often be met with sufficiently pure for toxicological investigations.

The other re-agents required are usually free from arsenic, and the paper may be tested by treating with nitric acid, saturating with sodium carbonate, evaporating to dryness, fusing the residue, treating with sulphuric acid, and testing the solution for arsenic as described at page 41.

ANTIMONY.

The presence of this metal, if unaccompanied by others forming dark coloured sulphides, is generally recognised at once by the orange red colour of the precipitate formed by hydrosulphuric acid. If collected on a filter, washed with water and treated with ammonia, the arsenious sulphide will dissolve, and almost the whole of the antimonious sulphide remain behind; it may be dissolved in hydrochloric acid and examined by tests described at page 43.

Any antimony that may have been dissolved by the ammonia will remain as antimonate after fusion with sodium nitrate and washing with water.

The characters of antimoniuiretted hydrogen, and of the spots produced by its imperfect combustion, have been already described.

TIN.

Salts of this metal are poisonous, but are not often employed for criminal purposes. If any salt, such as those used by dyers, has to be sought for in organic mixtures, the process previously described may be adopted, the precipitated sulphide which will be of a dirty yellow colour, it may be fused with potassium cyanide, and the resulting metallic bead treated with hydrochloric acid and the solution tested for tin as described at page 39.

BISMUTH.

The sulphide is soluble in nitric acid, also in strong hydrochloric acid, the solution evaporated to dryness yields a residue which is decomposed on the addition of water with separation of a white subsalt insoluble in tartaric acid. The salts of bismuth can scarcely

be reckoned among the poisons. Several cosmetics consist of subsalts of bismuth and some are composed entirely of lead carbonate; the soluble salts of lead are not decomposed by water, and the lead chromate is soluble in potassium hydrate while the bismuth chromate is not.

ZINC.

Salts of zinc are not often employed as poisons for criminal purposes, but accidents have happened from the accidental use of the sulphate and chloride. In the preceding process for the extraction of arsenic and other metals, the zinc will be contained in the filtrate from the precipitated sulphides, from which it may be thrown down by ammonia. The precipitate will usually be of a greenish colour from presence of iron, it may be dissolved in hydrochloric acid, the solution heated with a little nitric acid, precipitated by excess of ammonia, filtered, and the filtrate tested for zinc as described at pages 28-29.

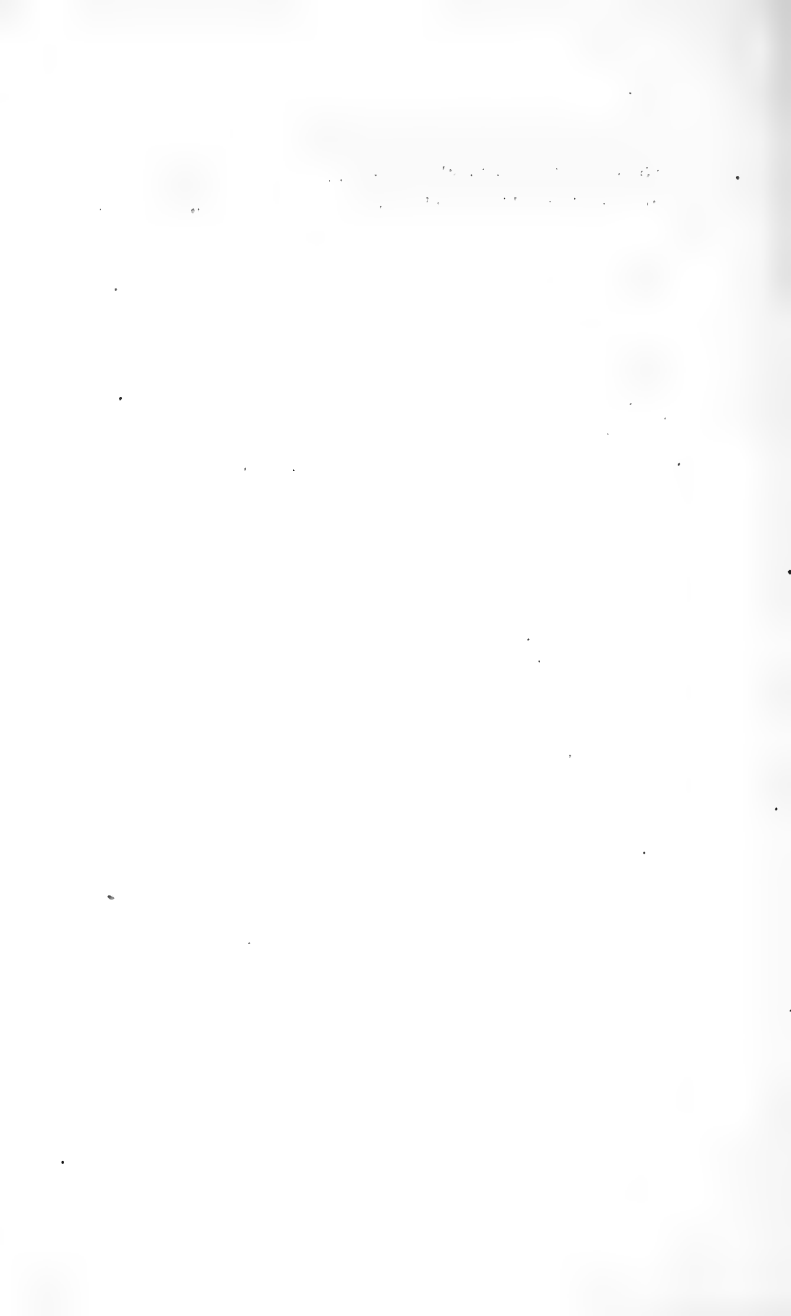
MERCURY.

The precipitated sulphide is black, insoluble in nitric acid if previously well freed by washing from hydrochloric acid; soluble in nitro-hydrochloric acid, forming a solution in which mercuric oxide may be detected by the tests described at page 35.

The precipitate when dried may also be heated with sodium carbonate in a reduction tube and a sublimate of metallic mercury obtained.

It must be remembered that calomel (mercurous chloride) will be converted during the process into corrosive sublimate (mercuric chloride), which will of course give the reactions of mercuric oxide. The mercury may perhaps best be detected in a solution acidified by hydrochloric acid, by the introduction of a piece of gold wire, round which some strips of tin foil have been wound; a grey deposit on the portions of the exposed gold wire will indicate mercury; the stains are removable on the application of heat.

In cases of poisoning by corrosive sublimate, small particles of the salt may often be found in the folds of the stomach, and these when heated with sodium carbonate in a reduction tube will yield a sublimate of metallic mercury.





COPPER.

If precipitated as sulphide from the decomposed organic mixture, the black sulphide will remain undissolved when treated with ammonia, it may be dissolved in nitric acid and the ordinary tests for copper applied.

Sheele's green (copper arsenite) gives a red residue when heated with potassium hydrate and a solution in which arsenious acid may be detected.

Heated in a reduction tube with dry sodium carbonate and charcoal or potassium cyanide, it gives a ring of metallic arsenic which may be recognised by the tests mentioned at page 41.

All compounds of copper when moistened with hydrochloric acid and exposed to the outer flame of the blowpipe, produce a blue or green colour.

LEAD.

This metal will be precipitated as black sulphide by the continuous action of hydrosulphuric acid, insoluble in ammonia or ammonium sulphide, but soluble in hot nitric acid of moderate strength, leaving more or less of a white residue of lead sulphate. If very strong nitric acid be employed the sulphide is entirely converted into sulphate which remains undissolved. It may be recognised by its solubility in hot hydrochloric acid, and by being reduced when heated before the blowpipe if mixed with sodium carbonate and potassium cyanide. In solution it may be recognised by the tests described under Lead.

ORGANIC POISONS.

HYDROCYANIC ACID.

This acid and the potassium cyanide often act as poisons when used either purposely or accidentally. Potassium cyanide has been employed instead of potassium carbonate in making an effervescing drink, and the cyanide used by photographers has given rise to many fatal accidents. Oil of bitter almonds contains the acid when in its crude state and has often been used as a poison. Peach kernels, bay leaves and various other substances yield hydrocyanic acid when distilled, especially if allowed previously to partially ferment. The amygdaline contained in them does not seem of itself to be poisonous, unless decomposition has set in. The root of the *Iatropha Manihot* from which tapioca is obtained seems to contain the acid or some substance yielding it, which is dissipated in the drying process adopted in preparing cassava and tapioca.

Nitrobenzol now extensively used as a substitute for oil of bitter almonds has been found to be a virulent poison, but is entirely free from hydrocyanic acid.

If the acid or salt is in a pure state the various tests described at page 52 may be applied, but if mixed with organic matter, as in the contents of the stomach the acid must be distilled off; tartaric acid having been added if the potassium salt is suspected. With thick liquids this process is attended with some difficulty, the best method is to heat the mass in a retort connected with a receiver or condenser and to pass steam into the retort by means of a bent tube reaching nearly to the bottom. The distillate may then be examined by the proper tests and the most minute trace of acid detected. Usually hydrocyanic acid escapes very rapidly from the body, easily recognised by its peculiar odour, and hence after a few days it may happen that no trace of it can be detected. By the above process of separation the writer has detected its presence after thirteen days interment.

The acid may also be detected without having recourse to distillation, by suspending over the suspected mass contained in a dish and

acidulated with tartaric acid, a watch glass or capsule moistened with silver nitrate or ammonium sulphide, covering the whole with a bell-jar and allowing to stand for some hours. The silver cyanide or ammonium sulphocyanate produced, if hydrocyanic acid is present, may then be examined by the proper tests.

ESTIMATION OF THE STRENGTH OF HYDROCYANIC ACID.

As the officinal acid is very apt to deteriorate and diminish in strength, it is of much importance to be able to determine it, for which purpose two methods may be adopted.

1. The acid is fully precipitated by silver nitrate, the precipitate collected on a weighed filter, washed, dried and weighed. The excess of weight over that of the filter gives the quantity of silver cyanide, every five grains of which indicate one grain of hydrocyanic acid, the molecule of which may be represented by 27 while that of the cyanide is 134. The latter number divided by 5 gives 26·8 very nearly equal to 27.

2. A much more expeditious process is by means of a standard solution of silver nitrate, the use of which depends on the following facts: When potassium cyanide is added to a solution of silver nitrate a precipitate of silver cyanide is formed which dissolves in excess of the precipitant forming the double cyanide $K\text{Cy}$, $Ag\text{Cy}$. This compound will always be formed whatever other acids may be present. If reversing the experiment silver nitrate be added to potassium cyanide containing (say) some chloride, no precipitate will be formed until the whole of the cyanogen present has been used up in forming the above salt; after that any excess of the nitrate will produce a permanent precipitate of chloride. As two atoms of cyanogen are present in the above salt, it is clear that two molecules of hydrocyanic acid neutralised with potash would exactly react upon one molecule of silver nitrate; the numbers representing these molecules being 54 and 170.

The process then is conducted as follows: 54 grains of the acid under examination are mixed with excess of potassium hydrate with a little sodium chloride; 170 grains of silver nitrate are dissolved in water contained in a burette divided into 100 parts. The solution of silver salt is added gradually with diligent stirring until a permanent precipitate or opalescence is formed, and the number of degrees

used read off. If 100 measure, *i. e.*, the whole had been used, then the acid must have been absolutely pure containing 100 per cent. of H Cy, but as in practice we never meet with such acid, it is better to use 17 instead of 170 grains of silver nitrate, a permanent precipitate after the use of 100 measures would then indicate 10 per cent., after 10 measures 1 per cent., and after 1 measure 0.1 per cent. Supposing 25 measures of such solution had been used before a permanent opalescence had been produced, but on the addition of a drop more a milkiness were produced not removable on stirring, then we should conclude that the acid contained 2.5 per cent. of pure hydrocyanic acid. This process is far preferable to the one above described, as it may be completed in a few minutes, while the other requires many hours.

OIL OF BITTER ALMONDS

The poisonous property of this oil in its crude state is owing to the presence of hydrocyanic acid which may be detected by the usual tests.

NITROBENZOL.

This substance is now extensively used as a substitute for the above oil in perfumery, and several accidents have happened from its use by swallowing or inhalation, the results appearing after a considerable lapse of time. The substance suspected to contain it may be distilled, the distillate shaken with ether which dissolves up the nitrobenzol, the ethereal solution evaporated till all ether is expelled and mixed with a little zinc and sulphuric acid, by this aniline will be produced which of course combines with the acid. The solution is treated with excess of potassium hydrate, and the whole shaken with ether which dissolves the aniline. The addition of ferric chloride to this solution will produce a fine purplish violet colour.

OPIUM.

This substance may be often detected by its smell, and by the chemical test for meconic acid rather than by those for morphine.

Ferric chloride added to a solution of meconic acid or to a light coloured solution of opium, produces a red colour which is not destroyed either by heating or by the addition of a solution of mercuric chloride. It is thus distinguished from acetic and sulphocyanic acids.

colic
heemic
isopropylamine } Red color
with
 Fe_2Cl_6
Not destroyed by heat, not by a sol. of HgCl_2
Not destroyed by heat or by HgCl_2
Destroyed by a sol. of HgCl_2 but not by boiling.

In organic mixtures, the meconic acid may be precipitated by lead acetate, and the washed precipitate decomposed by a little dilute sulphuric acid. The filtrate from this may be tested with ferric chloride.

VOLATILE ALKALOIDS.

The volatile alkaloids, nicotine and coniine can be distilled over from substances containing them by boiling with water, some strong alkali must be added if acids are present. To separate the alkaloid in a pure state the distillate must be neutralised with oxalic acid, evaporated to dryness, digested with spirits of wine, which dissolves the salt of the alkaloid and leaves any ammonium oxalate that may be present. The solution is evaporated, distilled with potassium hydrate, and the distillate shaken with ether which dissolves the alkaloid, and leaves it as an oily liquid on spontaneous evaporation.

NICOTINE.

Remains as a colourless or yellowish liquid, which on heating evolves white fumes smelling strongly of tobacco.

Platinic chloride produces a yellowish flocculent precipitate in an aqueous solution of nicotine, chlorine water produces no change.

The alkaloid is easily soluble in water.

CONIINE.

When heated it gives off a very strong pungent repulsive odour, and has a very acrid and disagreeable taste. It is exceedingly poisonous.

Platinic chloride produces no precipitate in aqueous solutions.

Chlorine water produces a strong white turbidity.

The alkaloid is difficultly soluble in water.

FIXED ALKALOIDS.

These cannot be distilled over with water.

MORPHINE.

This alkaloid is distinguished from all the following by being precipitated from solutions of its salts by potassium hydrate, but re-dissolved by excess.

Morphine and its salts give with nitric acid a red colour, destroyed by reducing agents, such as stannous chloride, sulphurous acid, sulphites, &c.

With ferric chloride a green or bluish green colour is produced.

Iodic acid produces a yellow colouration caused by separation of iodine, which may be detected by the addition of starch paste. Various other bodies produce the same colouration; but while in them it is destroyed by ammonia, it remains unchanged when caused by morphine.

Other tests are of comparatively little value.

The alkaloid when freshly precipitated is somewhat soluble in ether, and hence may be extracted by shaking a solution supersaturated by some base with ether. If allowed to stand and become crystalline it is quite insoluble in that liquid. This fact is of importance in testing for morphine in poison cases.

NARCOTINE.

This alkaloid, with quinine and cinchonine, form a group which is distinguished by the salts giving a precipitate with potassium hydrate insoluble in excess; the salts are also precipitated by hydric sodium carbonate (bicarbonate of soda), even from acid solutions.

The salts are decomposed by ammonia or alkalic carbonates, and the precipitate is easily dissolved by shaking with ether; the ethereal solution on evaporation leaves the pure alkaloid.

Nitric acid dissolves it, and produces a yellow colour on heating. Narcotine dissolves in sulphuric acid to a colourless or very feebly yellowish liquid; the addition of a most minute trace of nitric acid produces a red colour.

QUININE.

Alkalies and alkalic carbonates produce a white precipitate in salts of quinine which after a time becomes slightly crystalline, insoluble or nearly so in excess of the precipitate, but easily soluble on shaking with ether, when two distinct layers are formed, the upper being an ethereal solution of the alkaloid.

Hydric sodium carbonate produces an immediate precipitate if the quinine be present in not less than one part to the hundred of acid and water.

Chlorine water and ammonia, added to a solution of quinine, produce a fine green colour.

Chlorine water and a little potassium ferrocyanide, added to solution of quinine with the subsequent addition of a few drops of

ammonia, produce a fine red colour passing into brown, destroyed by acid and reproducible by ammonia.

Concentrated sulphuric acid dissolves quinine and its salts; on heating a yellowish colour is produced, which after a time passes into brown.

Quinine itself, as well as its salts, is intensely bitter to the taste.

CINCHONINE.

Alkalies and alkalic carbonates produce in dilute solutions a white highly crystalline precipitate of cinchonine, insoluble or nearly so in excess of the precipitant, and also insoluble in ether, by which test it is easily distinguished from quinine. The precipitate is easily soluble in boiling alcohol.

Hydric sodium carbonate acts in the same way.

Chlorine water and ammonia produce no green colour.

Chlorine water with potassium ferrocyanide and ammonia produce no red colour.

Concentrated sulphuric acid dissolves cinchonine and its salts; on heating a brown or even black colour is speedily produced, therein differing from quinine.

The salts of cinchonine are soluble in water and bitter to the taste, but the alkaloid itself being almost insoluble in water is very nearly tasteless, hence its use in the so-called *sweet quinine*, which contains no quinine at all, but is only a mixture of cinchonine with some saccharine matter.

SALICINE.

This substance though not an alkaloid may be here mentioned, as it is sometimes used as an adulteration of quinine and its salts, possessing a bitter taste and somewhat similar though weaker febrifuge qualities. Its presence may be detected by the addition of sulphuric acid, when a red colour is produced, especially after gentle heating.

Also by distilling with a little dilute sulphuric acid and potassium chromate, when a distillate is obtained giving a blue-violet colour with ferric chloride.

Also by giving a clear solution with dilute sulphuric acid, which becomes turbid on boiling from formation of insoluble *saliretine*;

the solution contains the quinine and grape sugar, which latter may be detected by heating with cupric sulphate and potassium hydrate. (See Sugar)

NOTE.

Quinine and its salts can scarcely be considered as poisons, but their constant use as medicinal agents renders their introduction among the alkaloids necessary. The following remarks on possible adulterations of its salts may not be without value.

Starch may be detected by boiling with water and adding tincture of iodine, when a blue colour will be produced. Also by the blackening action of sulphuric acid. Also by the formation of sugar by boiling with dilute sulphuric acid.

Sugar may be detected by boiling for a few minutes with dilute sulphuric acid, adding cupric sulphate and excess of potassium hydrate and again heating, when red cuprous oxide will be formed. It can also be detected by precipitating the quinine by ammonia and observing the sweet taste of the filtrate.

Quinine and its salts blacken when heated on platinum foil, the charcoal requiring long continued heat to cause it to burn away; any permanent residue of a white or greyish colour will indicate an adulteration of *gypsum* or some *earthy matter*.

The action of ether on quinine may be employed as a means of distinguishing it from cinchonine, together with the other tests above described.

STRYCHNINE.

This alkaloid as well as brucine and veratrine is precipitated from its solutions by potassium hydrate but is insoluble in excess, it is not precipitated by hydric sodium carbonate. By the latter test this group of alkaloids is distinguished from the preceding.

Potassium hydrate and sodium carbonate produce a precipitate which under the microscope appears highly crystalline, insoluble in excess of the precipitants.

Ammonia produces a precipitate soluble in excess but separating again after a time in the form of needles.

Hydric sodium carbonate produces a precipitate in neutral solutions immediately, in acid solutions only after a time.

Potassium chromate and sulphocyanate produce precipitates in solutions of strychnine which are more or less crystalline according to the state of dilution.

Nitric acid added to dry strychnine produces no colour if the alkaloid is pure ; but usually a red colour is observed owing to the presence of brucine.

Sulphuric acid dissolves pure dry strychnine without colouration, if to this solution an oxidising agent be added, such as a chromate, manganese dioxide or lead dioxide, a beautiful but evanescent bluish purple colour will be produced, changing rapidly to red. The chromate may be used in solution, only a small quantity being added, or in the solid form, the crystal being moved through the solution will produce purple streaks. The reaction is prevented by the presence of very small quantities of impurities, hence the vessels employed must be perfectly clean and the strychnine pure. The evanescent purple colour is characteristic.

The action of a solution of strychnine salts upon small frogs may also be employed as a test. In from a quarter to half an hour tetanic convulsions will be produced ; the animal should be fully immersed in the solution.

BRUCINE.

Does not often come under notice as a poison, in its reactions it closely resembles strychnine, but gives a deep red colour with nitric acid, and no purple with chromic acid, only a pink changing to yellow. The red colour produced by nitric acid is not changed by reducing agents.

VERATRINE.

Nitric acid forms resinous lumps which dissolve to a colourless solution.

Sulphuric acid also forms resinous lumps which dissolve to a faint yellowish fluid, changing to reddish yellow, and finally to deep blood red. The colour disappears after some hours. This test seems characteristic.

Veratrine and brucine when occurring in a pure state may be at once distinguished from all the other common alkaloids by the action of a few drops of *pure* sulphuric acid. Veratrine gives a

yellow colour changing to blood red. Brucine gives a rose colour changing after a time to yellow, the rose colour is very characteristic.

Morphine and brucine give a red colour with nitric acid, destroyed by reducing agents in the case of morphine but not in that of brucine. It must be remembered that commercial strychnine often contains brucine. The action of sodium hydrosulphide on brucine, lately recommended, has not proved satisfactory in the writer's hands.

SEPARATION OF ALKALOIDS FROM ORGANIC MIXTURES.

The suspected substance is mixed with twice its weight of alcohol and about twenty grains of oxalic or tartaric acid, and gently warmed for some time. The liver and other solid organs may be cut up, moistened with the warm solution, pressed out, and the operation repeated several times. The alcoholic extract is evaporated to dryness in a water bath, extracted with water, again evaporated, and the operation repeated with alcohol and water several times. The aqueous solution may then be shaken with ether to remove colouring matter, as the salts of the alkaloids are not soluble in that menstruum. Some ammonia or sodium carbonate is added to alkaline reaction and the whole rapidly mixed with ether and well shaken. If morphine has once become crystalline it is quite insoluble in ether. Amylic alcohol may also be used as a solvent, and dissolves morphine more readily. The solution in ether may then be drawn off by means of a pipette, and evaporated to dryness. If the residue appears impure it may be re-dissolved in a little dilute sulphuric acid, and the same operation repeated. In order to obtain as much as possible of the alkaloid on one spot, the solution may be poured drop by drop on to a heated capsule, and the appropriate tests applied to the residue.

Chloroform may also be used for extracting the alkaloid. It may be remarked that morphine is the most difficult to extract, its successful separation being the exception.



ALCOHOL.

It may sometimes be necessary to determine the presence of this substance in the contents of a stomach. The whole mass should be distilled either by itself or by means of the contrivance described under the head of hydrocyanic acid. The distillate should then be introduced into a small retort with some potassium bichromate and sulphuric acid; on applying heat the solution will become of a green colour owing to formation of chromic oxide, and the distillate will acquire a yellow colour on addition of potassium hydrate. Other parts of the body besides the contents of the stomach may be submitted to the same treatment.

CHLOROFORM.

May be separated by distillation and recognised by its smell. Chemical tests are scarcely applicable.

PHOSPHORUS.

This substance is not often employed as a poison, but accidents occasionally occur from its consumption either as rat poison or matches. In such cases the peculiar odour of phosphorus will be perceptible in the contents of the stomach, and the mass will be slightly luminous in the dark if gently warmed. To prove the presence of phosphorus the suspected substance may be mixed with dilute sulphuric acid and distilled, the vapours evolved conducted into a tube cooled by water, when a faint light will be seen at the mouth of the tube, and small particles of phosphorus will condense and may be received in a proper vessel and further tested by solution in nitric acid, &c.

U R I N E.

It is often of importance to determine the specific gravity of this secretion, for which purpose various instruments may be used. The simplest, and, at the same time, the most accurate plan is to attach a piece of glass, such as a moderate sized stopper to a piece of fine platinum wire or silk. After this has been weighed in air, its loss of weight in water must be ascertained, let this be called A. Then to ascertain the gravity of any sample of urine, determine the loss of weight in the urine = B. The specific gravity will be found by dividing B by A; the weight of the stopper in air and its loss in water may be scratched on the glass itself by means of a hardened file.

Healthy urine varies from 1003 to 1030 according as the experiment is made before or after the digestion of a meal, or after much water or other fluid has been taken. The average may be said to lie between 1015 and 1025. Its reaction is generally slightly acid, but if examined after meals it is sometimes neutral, on keeping for some time it becomes alkaline from formation of ammonia. Morbid urine is frequently strongly alkaline, and will sometimes effervesce on the addition of acid, the urea having been decomposed into ammonium carbonate.

Healthy urine deposits no immediate precipitate on cooling, but a deposit is not unfrequently observed in the night's secretion, which on the addition of the morning's urine either disappears or not. In the former case the deposit is probably ammonium urate, in the latter ammonio-magnesian phosphate, or some earthy salt.

UREA.

Healthy urine concentrated to about one-half or one-third and mixed when cold with an equal bulk of pure nitric acid, deposits plates of impure urea nitrate; if an excess of urea be present, the concentration need not be carried so far. The proportion varies from about $\frac{1}{165}$ in healthy, to $\frac{3}{100}$ in unhealthy urine. Oxalic acid may be used instead of nitric.

URIC ACID.

Exists in healthy urine to the extent of about 1 part in 1000, in unhealthy urine there is sometimes twice as much, in which case it is usually deposited as a reddish sediment, not dissolved on heating. It is seldom free from ammonium urate. The deposition is much assisted by the addition of a little hydrochloric acid. See fig. 3, plate 2.

To recognise the presence of free uric acid, the sediment should be boiled with a small quantity of water to dissolve out the urate, the residue will then be found to be soluble in potassium hydrate, and re-precipitated on addition of hydrochloric acid. Some of the precipitate being collected on a filter and washed, is removed into a white porcelain capsule and treated with a few drops of pure nitric acid. Effervescence takes place, and on carefully evaporating to dryness, a red colour is produced, which on the addition of potassium hydrate (after cooling) yields a fine purple colour. Care must be taken to drive off all trace of nitric acid, but not to heat so strongly as to char; when time is no object the operation is best conducted over a water bath.

HIPPURIC ACID.

This acid appears to be present in all urines especially in that of vegetarians. In certain diseases, such as chorea, its quantity increases considerably. It can be detected by evaporating a pint of urine to a syrup, acidulating with hydrochloric acid, shaking with ether, evaporating the ethereal solution and boiling the residue with a little water. On cooling, hippuric acid separates in feathery crystals. Its physiological relations are not well understood, and as it is found in the urine of herbivorous animals to a large amount it can scarcely be called a morbid constituent unless present in abnormal quantity.

SALTS.

Fresh and healthy urine contains only slight traces of ammonium salts, in disease the quantity is often largely increased. On evaporating urine and carefully incinerating, a residue is left amounting to about 12 or 15 in 1000, which yields to water alkalie sulphates, chlorides and phosphates. The insoluble portion consists principally of calcium and magnesium phosphates with slight traces of silicie

acid and alumina. These earthy salts are sometimes largely increased in quantity.

AMMONIUM URATE.

Is often present in morbid urine and is deposited on cooling. On applying heat it re-dissolves and the urine becomes perfectly clear. The deposit, which is usually of a reddish colour, may be collected, washed and gently warmed with potassium hydrate; it dissolves with evolution of ammonia forming a solution from which hydrochloric acid precipitates uric acid which can be recognised by the proper test. The deposit itself may at once be treated with nitric acid, and the above method of examination is applicable to calculi consisting of urate as well as to deposits. Occasionally sodium urate occurs.

The deposit if examined under the microscope appears in rounded grains without crystalline structure, if treated with a little hydrochloric acid small crystals of uric acid soon make their appearance. The sodium urate may be recognised by not giving off ammonia when treated as above and by tinging the blowpipe flame yellow. Its microscopic appearance is also characteristic. See fig. 8, plate 2.

MUCUS.

Is often found in morbid urine in large quantities, it forms a viscid sediment which, when shaken up, does not mix uniformly with the urine, but forms ropy masses in which frequently enormous quantities of the prismatic crystals of ammonio-magnesium phosphate are entangled, which render the mucus more opaque and cause it to resemble pus. Such urine however will give no precipitate with nitric acid or on boiling, while urine containing pus gives a slight precipitate. Urine containing mucus is often alkaline when passed, owing to the action of this substance on the urea. See figs. 10 and 11, plate 2.

COLOURING MATTER.

The red colour of urine may be owing to purpurine which readily attaches itself to ammonium urate, or to blood. The latter can be detected under the microscope, or by the usual tests for blood, and by the red colouring matter being insoluble in alcohol while purpurine is easily soluble. Various other colouring matters are occa-





sionally found in urine. It has been proved that all urine contains a substance allied to the glucosides, which when treated with dilute acids or by natural decomposition yields grape sugar and indigo blue; hence occasionally blue urine is met with. For figures of blood corpuscles see plate 2, fig. 12.

FAT AND CHYLE.

Urine containing these substances exhibits under the microscope numerous small transparent globules. See fig. 9, plate 2. If shaken with ether, the globules will be removed if consisting of fat, but will be unaltered if composed of chyle, they are also in this way distinguished from the fat globules in milk, which are very similar in appearance, the latter being covered apparently with a coating of some protein compound, are not dissolved by ether unless previously shaken with potassium hydrate. The ethereal solution may also be evaporated and the residue examined. The substance called kiestein observed after some days on the urine of pregnancy, seems to owe its peculiar appearance to the presence of crystals of the triple phosphate mixed with some organic matter.

SUGAR.

This substance has been proved to be present in small quantities in almost all urines, whether as a natural product or as a result of the decomposition of a glucoside. Occasionally it is present in abnormal quantity producing or characteristic of the disease called *diabetes mellitus*. The amount of grape sugar in the urine is sometimes enormous, and occasionally immediately previous to decease, vanishes altogether.

Diabetic urine has usually a high specific gravity, sometimes as high as 1055, usually from 1030 to 1045. The smell of the urine is usually different from that of the healthy secretion and generally forms a white scum on the surface after standing.

Trommer's test. The urine is mixed with a few (8-10) drops of solution of cupric sulphate, potassium hydrate is then added till the blue precipitate first formed is dissolved and a clear solution obtained. The whole is then gently heated, not boiled, when a yellow or red precipitate will be formed. Occasionally no precipitate is produced, but only a red colour. It is always well to make a corresponding experiment with healthy urine.

This test, although not absolutely infallible, is probably the best for general use, as that of Maumené depending on the use of stannic chloride is not available unless in well-appointed laboratories.

If the urine be mixed with half its volume of potassium hydrate and boiled for a short time, it will become deep yellow or brown, which is not the case with healthy urine.

If the urine be mixed with a few drops of solution of bismuth nitrate, sodium carbonate added to alkaline reaction, and the whole boiled for a few minutes, the mixture assumes a drab colour. The absence of albumen must be previously demonstrated.

The fermentation and torula tests may be omitted as not adapted for use by the readers of this small work; they are referred to Bloxam's edition of Bowman's Medical Chemistry, or Lehmann's book on Physiological Chemistry.

For experiments to illustrate the action of the above tests, a little honey may be added to urine, and comparative trials instituted with and without sugar.

ALBUMEN.

In Bright's disease and many others, the urine often contains albumen, but the physical characters of the secretion vary so much that no general rule for guidance can be laid down.

The albumen is coagulated by heating the urine to a temperature of $76-77^{\circ}$ c. and the precipitate is then perfectly insoluble in water, but readily dissolved by potassium hydrate.

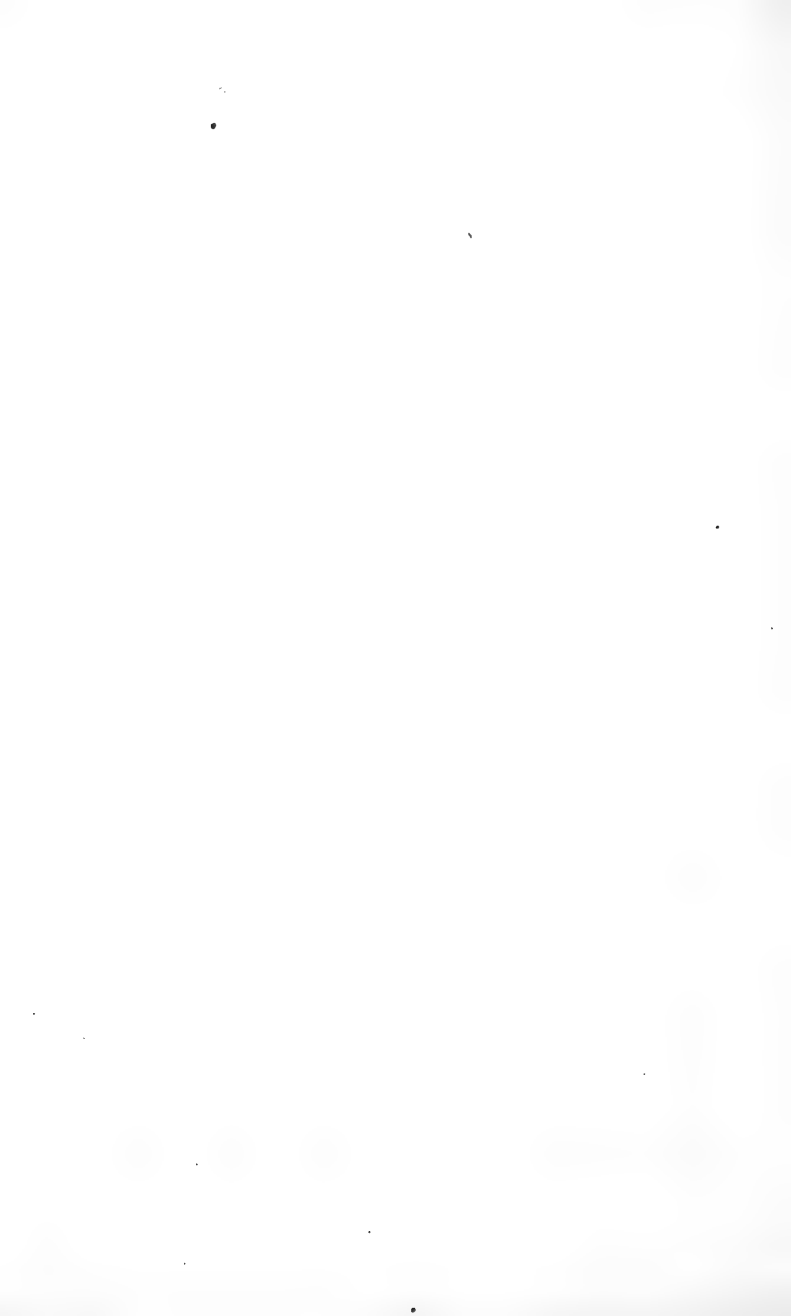
It is precipitated by nitric and hydrochloric acids, but not by acetic or tartaric.

It is precipitated by mercuric chloride (corrosive sublimate), by potassium ferro and ferri-cyanide and by many other metallic tests. The mercuric compound has been said to be soluble in excess of albumen, hence in using white of egg as an antidote in cases of poisoning by corrosive sublimate an excess thereof should be avoided.

If a precipitate is formed on boiling, it will be better to add a few drops of nitric acid, as the same result may be produced by earthy precipitates; in presence of albumen the precipitate will remain undissolved.

The formation of a very faint precipitate may arise from the presence of pus in the urine.

Maumené's test



If the urine be alkaline no precipitate will be formed on boiling, it should be carefully neutralised before heating.

The formation of a precipitate both by nitric acid and by boiling is conclusive as to the presence of albumen.

In urine containing blood, albumen will naturally be found, but the presence of blood corpuscles may generally be detected under the microscope, if sufficient power (400) be used. (See plate 2, fig. 12.)

BILE.

Urine suspected to contain bile, which gives to it a more or less yellowish brown colour, should be boiled to separate any albumen that may be present and concentrated by evaporation. A strong solution of a few grains of cane sugar is then added, and sulphuric acid gradually, with constant shaking, until the mixture becomes hot. About two-thirds of the acid will be required to produce the characteristic *purplish red* colour. Another method is to add a little sugar and sulphuric acid to the boiled and filtered urine and to evaporate over a water-bath nearly to dryness.

This is the only test that can be safely relied on. Biliary calculi or gall-stones are usually composed of cholesterin more or less coloured. Boiling ether extracts the cholesterin from the powdered stones and deposits it in white crystalline scales on cooling.

FIGURES OF URINARY DEPOSITS.

COPIED FROM BLOXAM'S EDITION OF BOWMAN'S MEDICAL CHEMISTRY.

Fig. I.—A drop of the urine allowed to stand some short time on a glass plate may exhibit under the microscope, with a power of 200 diameters, the appearance represented in this figure, that is stellate crystals, which disappear very rapidly on the addition of a drop of acetic acid—Ammonium-magnesian phosphate.

Fig. II.—These crystals are often observed in urine, especially in that which is diseased, often inclosed in a precipitate of mucus—they are easily soluble in acetic acid, and of the same composition as those depicted in No. I, although the form is very different. In cases of disease the latter form is more generally apparent. The composition appears to be the same.

Fig. III.—Uric acid exhibits a number of forms, some of which are depicted in the accompanying plate. The acid may be

recognised by its solubility in caustic potassa, by its reprecipitation by hydrochloric acid, and by the red colour produced by the action of nitric acid on the separated precipitate. The addition of potassium hydrate to the evaporated solution produces a blue or purple colour. The uric acid crystals are insoluble in dilute acids.

Figs. IV. & V.—Octohedral crystals with distinct crosses, or some modifications of the dumb-bell form, will indicate calcium oxalate. The crystals are insoluble in acetic but soluble in hydrochloric acid.

Figs. VI. & VII.—If the crystals are multangular plates exhibiting the form shown in figure 6, insoluble or nearly so in water and dilute acids, but readily soluble in ammonia, the solution leaving on evaporation hexagonal plates shown in 7, they are probably cystine. (The writer has never had an opportunity of examining these crystals, while the correctness of all the other figures has been repeatedly tested.)

An amorphous sediment, insoluble when warmed, but easily soluble in acetic or hydrochloric acid may probably be calcium phosphate.

If dissolved on warming and reprecipitated on cooling it may be ammonium or sodium urate, the latter

Fig. VIII. often has the form exhibited in Fig. 8.

Fig. IX.—Small round globules, easily removable by shaking with ether, will indicate fatty matter.

Chylous matter will be indicated by similar globules, partly removable by ether, but leaving small amorphous albuminous particles. The albumen may be further detected by proper tests.

Fig. X.—Round particles apparently granulated and entangled in tenacious stringy masses, which do not break up and mix uniformly with the liquid on agitation, will probably be mucus 10 a. Epithelial scales are represented at 10 b.

Fig. XI.—If the particles are round and granular, not held together by any tenacious matter, but floating freely in the liquid, they are probably owing to the presence of pus.

Fig. XII.—Blood globules, colour destroyed by chlorine water.

Fig. XIII.—Spermatozoa showing the presence of semen.

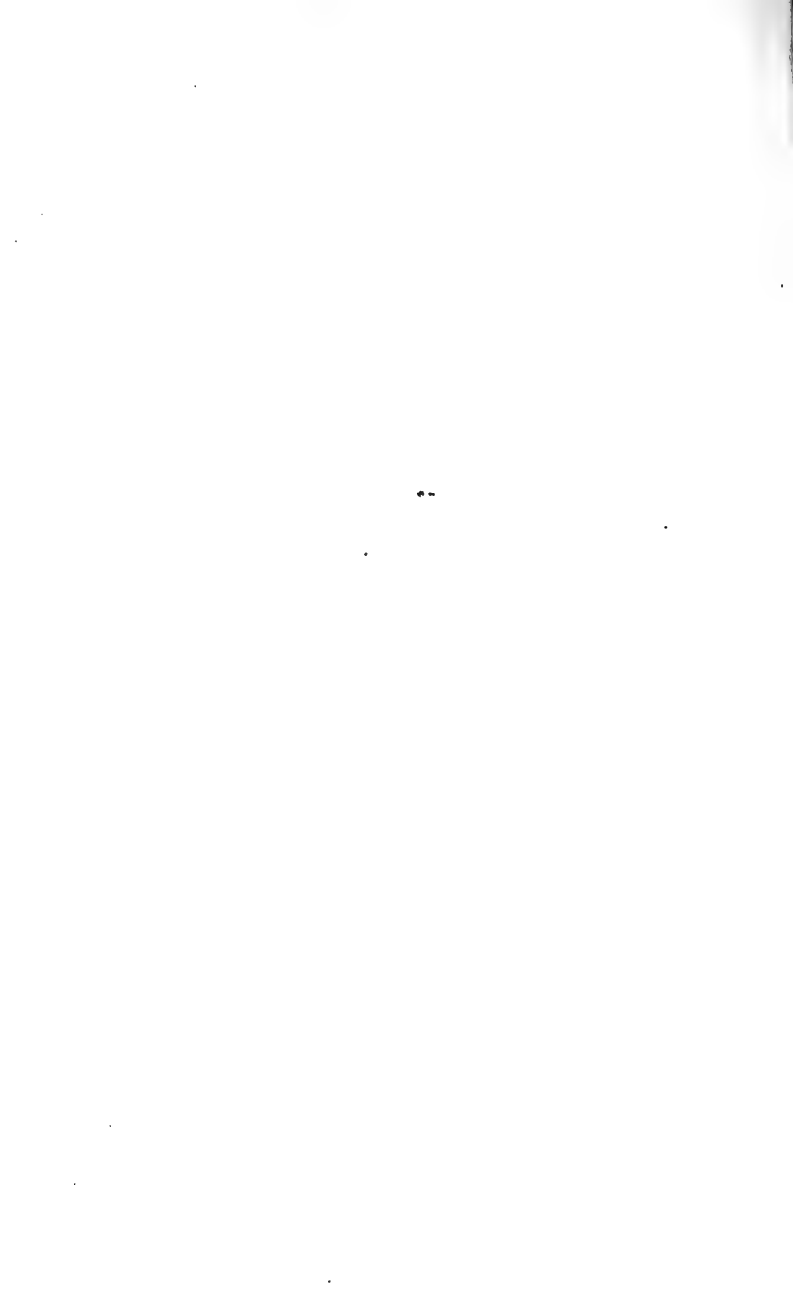


Fig. XIV.—Pus globules seen under a high power (400 diameters) both before and after treatment with acetic acid, which renders them more transparent and exhibits the internal nuclei.

Fig. XV.—Crystals of sodium chloride, easily soluble in water.

Fig. XVI.—Crystals of sodium chloride resembling cystine.

Fig. XVII.—Crystals of cystine from ammoniacal solution.

Fig. XVIII.—Crystals of calcium oxalate seen when dry.

NOTE.—The above figures have been copied after repeated confirmation, except in the case of cystine, from Bloxam's edition of Bowman's Medical Chemistry.

MILK.

Medical men may often be required to give an opinion as to the healthy or diseased condition of human milk, but it does not appear that there are any chemical tests by which a diseased condition can be detected unless very abnormal. Recourse must be had to the microscope, a deficiency of fat globules, and the presence of large colostrum or pus globules, especially if of a red colour, and of red fibrinous particles, will indicate an abnormal condition. The lactometer for measuring the quantity of cream has been recommended as a means of determining the value of the milk, but the instrument does not always yield indications that can be relied on, and the nutritive powers of the secretion do not depend entirely on the amount of fatty matter present.

URINAR : CALCULI.

All calculi blacken more or less and evolve an odour on the application of heat, the mulberry calculus (calcium oxalate) least of all. With cystine the smell is very peculiar.

They may be divided into two classes.

1. Those which are perfectly destructible by heat, or leave only a minute trace of ash.

Uric acid, ammonium urate, cystine, xanthine.

2. Those which are imperfectly destructible by heat, leaving an earthy or alkaline residue after the separated carbon has been burnt off.

Calcium oxalate and urate, sodium urate, calcium phosphate, ammoniaco-magnesian phosphate, fusible calculus.

The first two leave a residue of calcium carbonate or oxide ; the third sodium carbonate ; the fourth calcium phosphate ; the fifth magnesium phosphate ; and the sixth a mixture of these two latter salts.

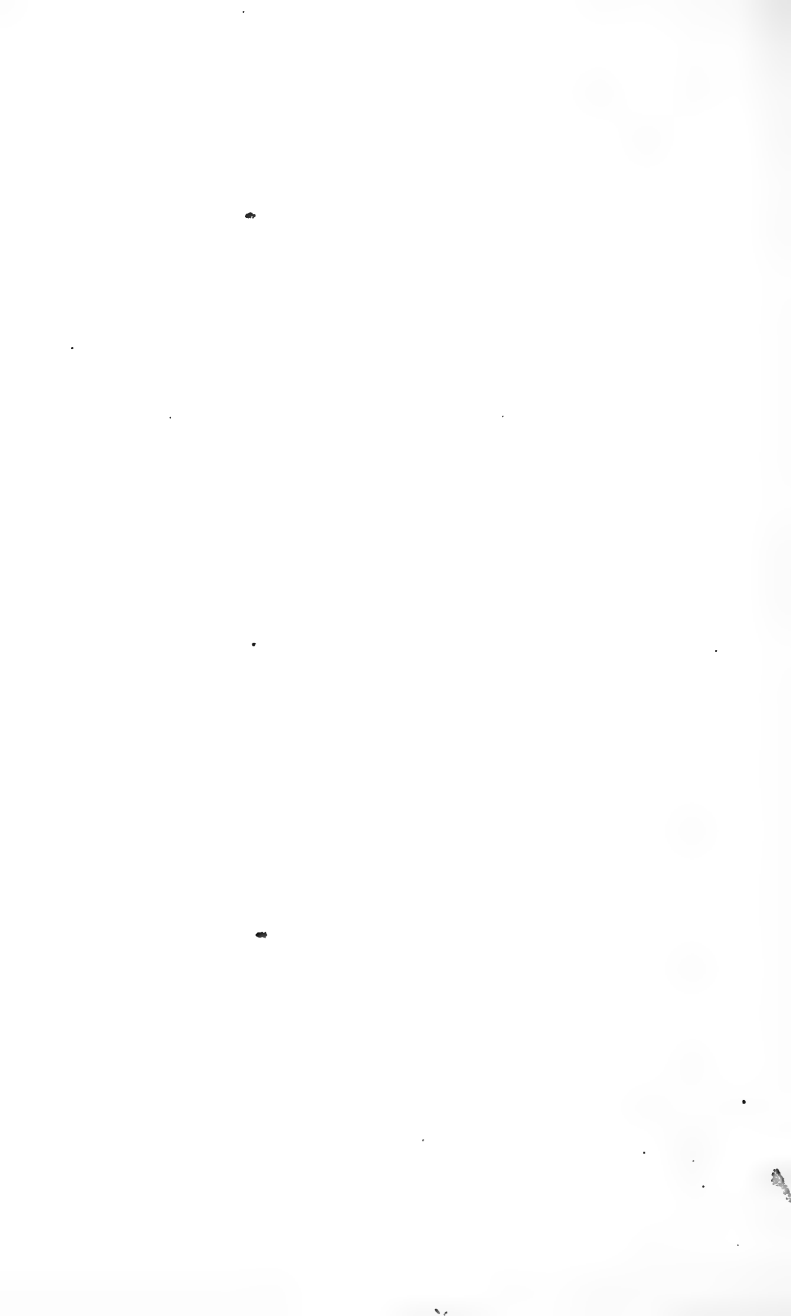
Urinary calculi are frequently composed of two at least, of the above substances, the kernel is often different from the external coating, and hence the various parts must be examined separately ; they almost all contain traces of uric acid.

The calculus in fine powder is boiled for some minutes with water, filtered and the solution evaporated to a small bulk, a portion is evaporated to dryness, and the residue, if any, may be ammonium sodium or calcium urate. The ammonium may be detected in another portion by boiling with potassium hydrate, the calcium by acetic acid and ammonium oxalate, and the sodium by adding hydrochloric acid, evaporating to dryness and burning with alcohol. The cubical crystals may also be observed.

The washed residue is boiled with dilute hydrochloric acid, the presence of the rare calcium carbonate will be indicated by effervescence. If any residue remains it must be thrown on to a filter, washed and tested for uric acid as described at page 101.

The hydrochloric solutions may contain lime from the carbonate, oxalate, cystine and the phosphates. Excess of sodium acetate being added, a precipitate may be formed of oxalate and perhaps of cystine, which however occurs very rarely. The precipitate may be washed and dried, it then dissolves in hydrochloric acid *without* effervescence, but after being dried and rather strongly heated *with* effervescence ; calcium oxalate.

To the solution separated from the oxalate, excess of ammonium oxalate is added, which throws down all the lime, the precipitate being filtered off and the filtrate tested with oxalate to prove that all lime has been got rid of, will give a white precipitate on the addition of ammonia, if ammoniaco-magnesian phosphate be present. A mixture of these two phosphates forms the fusible calculus, which melts easily before the blowpipe flame. The phosphoric acid can often be detected by moistening the burnt calculus with silver nitrate, when a yellow colour is produced, or by dissolving in a very little nitric acid, adding the nitrate and then the ammonia very carefully. Also by ammonium molybdate.





The ammonia in the last named phosphate can of course be detected by heating with potassium hydrate. Cystine dissolves in ammonia, and the solution yields on evaporation hexagonal tables (see fig. 7). A calculus of cystine may be easily recognised by this test and by the peculiar smell evolved on heating. Urine containing cystine has an aromatic odour when fresh, but is very offensive when decomposition commences. Cystine when boiled with potassium hydrate and mixed with a lead salt, produces a black colour from presence of sulphur; the formula is apparently $C^3 H_6 N O^2 S$.

Xanthine or Xanthic oxide $C^5 H^4 N^4 O^2$ is very rare, it dissolves in potassium hydrate, and is reprecipitated by hydrochloric acid, but is distinguished from uric acid by giving a yellow colour with nitric acid. It has been found in healthy urine and in many parts of the body.

The residue left on heating sodium urate will be found to be alkaline by its reaction on red litmus paper, and the same will be observed with calcium urate if very strongly heated. Both these salts occur usually in combination with other bodies and not independently.

BLOOD AND BLOOD STAINS.

The chemist may often be called upon to examine blood in a liquid form, or dried in stains on clothes or weapons. Blood sometimes occurs in urine in which it may be detected by its appearance under the microscope, see fig. 17, plate 2, and by the fact that the urine is coagulated or becomes turbid on the application of heat or nitric acid, owing to the presence of albumen.

If the blood, or what is supposed to be blood, forms a stain on any article of clothing or any other substance, such as a knife, axe, wooden handle, &c., &c., it should be allowed to soak in water for several hours, when if the stains were caused by blood, a reddish solution will be obtained. A blood stain on steel will generally peel off when gently warmed, while a stain produced by rust or acid will not do so. If a portion of the stain can thus be peeled or scraped

off by a knife, it may be heated in a small tube in the upper part of which a piece of moistened red litmus paper is placed; if the colour is turned to blue the presence of some animal matter containing nitrogen is probable; most vegetable substances, such as fruit stains, would have no action on red litmus, but would redden the blue paper.

To a portion of the red liquor obtained ammonia is added, which will produce no alteration in the colour if it be owing to blood, but will turn most vegetable colours blue or green.

Another portion is boiled, when the solution will become nearly colourless, and a dirty brown precipitate be formed; vegetable infusions are scarcely altered.

Nitric acid is added to another portion, when if blood is present a precipitate will be formed owing to the albumen.

Chlorine is passed through another portion when in presence of blood the liquid will acquire a faint greenish tint and a flocculent precipitate be produced. With vegetable infusions the colour is simply destroyed. The solution is then boiled until all smell of chlorine is lost; filtered and the filtrate tested with potassium sulpho-cyanate, if blood were present a red or faint pink colour will be produced owing to the presence of iron, the colour becomes more apparent on looking through the tube lengthwise.

The stains may be softened with dilute glycerine, and the red liquid examined under a powerful microscope, the blood corpuscles may be easily recognised, but it seems doubtful whether human blood (after being dried) can thus be distinguished from that of mammals.

A few drops of the solution may be mixed with a very little sodium chloride on a slide and evaporated over sulphuric acid, the addition of a drop of strong acetic acid and subsequent evaporation at 100°C will cause the formation of red crystals, visible on the addition of a drop of water.

If blood stains are very old or mixed with rust the hæmatine is often insoluble, in that case they may be digested with potassium hydrate, and the iron detected by the use of chlorine and sulpho-cyanate as above described. Various other tests have been proposed, many very valuable but not easily available.

MINERAL WATERS.

It may often be necessary to make a rough qualitative analysis of water supposed to possess medicinal properties when the following simple experiments may be made. A few ounces are boiled for an hour in a flask, adding distilled water occasionally to prevent concentration; the formation of a precipitate easily soluble in dilute hydrochloric acid will indicate the presence of carbonates held in solution by carbonic acid. If the precipitate is of a reddish colour ferric carbonate must have been present, the solution in acid may be mixed with ammonium chloride and ammonia added, the ferric hydrate will be precipitated, in the filtrate ammonium oxalate will throw down calcium oxalate, and in the filtrate from this sodium phosphate will after standing, produce a crystalline precipitate if any magnesium is present.

The presence of free carbonic acid may be detected by the precipitate formed on the addition of lime water. Hydrosulphuric acid by its smell and its giving a yellow precipitate with an acid solution of arsenious acid. Sulphates and chlorides by barium and silver nitrates. Calcium and magnesium as above described, and the alkalis when present principally as chlorides by evaporating to dryness with a slight excess of oxalic acid, heating to redness and extracting with water, the lime and magnesia remain undissolved.

For the detection of iodine and other rarer constituents the reader is referred to Fresenius.

ALKALIMETRY.

The determination of the real quantity of alkali in commercial soda, soda ash, sal soda and various other similar preparations of potassa is often of great importance, the process being called alkalimetry.

For this purpose an alkalimeter or graduated burette is required capable of holding 1000 grains of water and marked off into 100 divisions. Mohr's burette in which the drawn-out lower end is connected with a small dropping tube by means of a piece of vulcanised tubing, is the most convenient as it can be supported in a clamp attached to the retort stand and the flow of the acid stopped or regulated by a nipper-tap placed over the India rubber tube. A simple apparatus may be constructed from a glass tube about $\frac{3}{4}$ inch

in diameter and 16 inches in length, one end is closed by fusion and the open end furnished with a lip.

A portion of water weighing 50 grains is carefully weighed, introduced into the tube and its height marked by means of a file or diamond, the operation is repeated with fresh portions until 20 measures have been introduced. The process of weighing out so many quantities is rather tedious, and the operation not very accurate when water is employed owing to its adhering to the glass. When mercury is available 678.4 grains may be weighed out, introduced into a small tube and its height marked off, every trace of the metal can be poured into the burette and another portion measured off.

The divisions corresponding to 50 grains of water or 678.4 grains of mercury may then be divided into five smaller divisions by the eye, each of which will contain 10 grains of water. The larger divisions are numbered 5, 10, 15, etc., from the top, by means of a writing diamond, or a common file heated to a dull redness, cooled by throwing into water and ground to a point. Any bubbles of air adhering to the tube during the operation should be removed by a thin wire.

A test acid must now be prepared, every division of which as measured by the burette will exactly neutralise one grain of soda. Four parts of sulphuric acid are mixed with twenty parts of water and allowed to cool. An ounce or more of pure sodium bicarbonate is heated strongly for half an hour, to convert it into carbonate, and 170.6 grains of this salt (containing exactly 100 grains of soda) weighed out and dissolved in three or four ounces of water, with the addition of a few drops of solution of litmus sufficient to render the solution distinctly blue; to this the dilute acid must be poured from the burette filled up to the top mark, as long as effervescence takes place and until the blue colour changes to bright red. The addition may be made rather rapidly at first, but as soon as a violet colour appears, with more caution heating between each addition. The violet colour is caused by carbonic acid, and changes to blue when the acid is expelled by heat. Towards the end the acid must be added by single drops, and as soon as the bright red colour is produced, the number of divisions read off. If exactly 100 divisions have been used the acid is of precisely the proper strength, but this is seldom the case with the above-mentioned preparations. Supposing 90 measures have been used, the acid is too strong and



must be diluted, which is easily done by pouring the acid into the burette up to the 10 division and filling up to 0 with water. Where only a moderate quantity of test acid is required this plan is sufficiently applicable, for larger operations a special mixing cylinder must be graduated.

If now a sample of soda or its carbonate has to be examined, 100 grains are weighed out and treated as above described with the test acid, supposing the crystallised soda salt were used, $21\frac{1}{2}$ measures would be employed, hence the 100 grains contain 21.5 per cent. of soda. The amount of dry carbonate may be ascertained by a simple calculation : $\text{Na}^2\text{O} : \text{Na}^2\text{CO}^3 :: 21.5 : x$; or $62 : 106 :: 21.5 : 36.7$.

Sodium baborate may be examined in the same manner, but when potassium salts are examined 151.5 grains must be used instead of 100, or the divisions read off at the end of the operation increased in the proportion of 62 : 94. In some samples there are contained both the carbonated and caustic alkali, in that case one experiment must be made as above to determine the whole amount of alkali present, and a second portion of 100 grains dissolved in water, precipitated with barium chloride, and the precipitate filtered off and washed as rapidly as possible. In the filtrate the amount of caustic alkali is determined.

When a sample does not dissolve perfectly the insoluble portion should be separated by filtration.

Sulphides and hyposulphites, which are sometimes present, may be destroyed by warming with a little potassium chromate.

ACIDIMETRY.

The normal solution, when only occasional experiments are required, may be made by dissolving 170.6 grains of pure sodium carbonate in water and filling the burette up to 0. This solution when well mixed will contain one grain of soda in each division ; 100 grains of the acid are weighed out, mixed with water and litmus, and the soda solution added until a violet tint is produced, which becomes blue on boiling.

A calculation must be made for each acid, as 62 grains of soda neutralise respectively 98, 63 and 36.5 of hydrated sulphuric, nitric and hydrochloric acids respectively.

MISCELLANEOUS EXAMPLES.

POTASSIUM IODIDE

May contain potassium carbonate, which is easily detected by the effervescence produced by the addition of dilute nitric acid and by the precipitate formed by calcium chloride. It may also be adulterated with potassium chloride, and perhaps at the present time with bromide, owing to the low price of this latter salt. To detect these a solution of the iodide should be fully precipitated by silver nitrate, the precipitate washed and treated in the cold with a moderate excess of ammonia, which will dissolve the chloride but leave most of the bromide, the residue may then be gently warmed with a large excess of ammonia, which will dissolve the bromide. These solutions, if acidulated with nitric acid, will yield precipitates if chloride and bromide have been present.

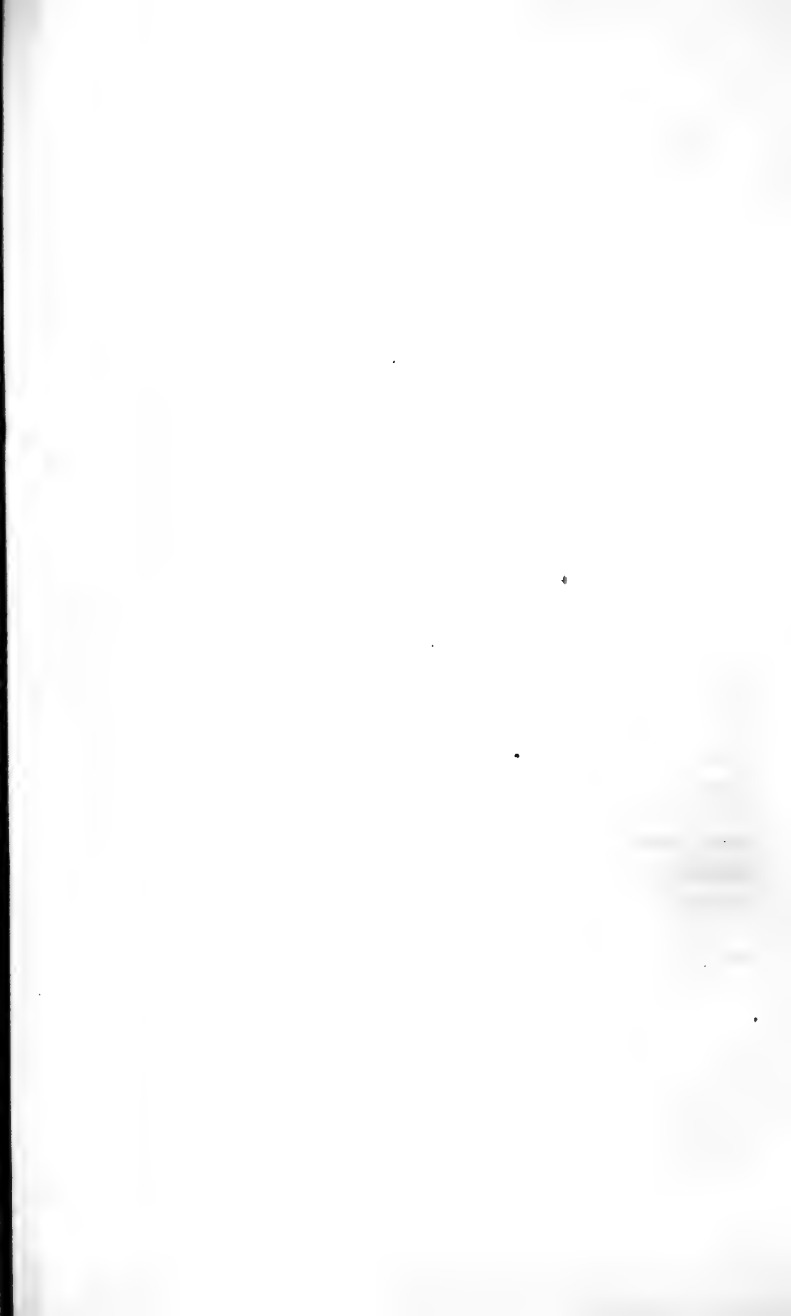
Potassium iodate is sometimes present, which often produces a yellowish colour in the otherwise perfectly white salt. It may be detected by the addition of tartaric acid, when a yellow or brown colouration will be produced, owing to the separation of iodine, which may be further recognised by the tests described under Hydriodic Acid.

MERCURIC OXIDE.

Is sometimes adulterated with red lead, which can be easily detected by heating strongly in a porcelain crucible, when the mercuric oxide will volatilise (as mercury and oxygen), while yellow lead oxide will remain, which may be dissolved in dilute nitric acid and detected by the proper tests for lead. It has been sometimes adulterated (?) by an admixture of brickdust, which could be detected by heating as above and digesting with dilute acid, when if the above impurity be present, an insoluble residue will remain.

ANNOTTO.

This colouring matter is sometimes used for colouring cheese and buns, and an adulteration of it once led to very serious results. Lead chromate was added, which can be easily detected by boiling.



with alcohol and hydrochloric acid, when a bright green solution will be obtained, in which chromic oxide can readily be detected. Orpiment or arsenious sulphide was added to the lead chromate or used as a substitute, and this can be best detected by the process described under the head of arsenic (Poisons).

CALOMEL.

Often contains corrosive sublimate, and every specimen used by druggists should be carefully examined for this poisonous body before being used in prescriptions.

It may be detected with the greatest ease by boiling the calome for a few minutes with water, filtering off and testing the filtrate with excess of hydrosulphuric acid. A precipitate which is white or orange until a large excess of the precipitant is used, indicates corrosive sublimate. Other tests described under mercury may also be employed. The colour of the sulphide produced by an excess of hydrosulphuric acid is black, and the precipitate when well washed is insoluble both in hydrochloric and nitric acids, but soluble in a mixture of the two.

LEAD CARBONATE.

This substance, which is so valuable as a pigment, is not unfrequently adulterated with barium sulphate, a salt which unless artificially prepared, is usually crystalline and possesses little or no covering property (body) when used as a paint. It may be easily detected by boiling the white lead with rather dilute nitric acid. If pure it should dissolve entirely. The solution might, however, contain lime if the carbonate had been used as an adulterant, which owing to its low specific gravity is not likely. In that case the lead may be precipitated by hydrosulphuric acid, the operation repeated until no further black precipitate is formed, and the filtrate tested for lime as described at page 26.

CHLOROFORM

Is sometimes impure from the presence of alcohol, which may be detected by warming with a little potassium chromate and sulphuric acid, when a green colour will be produced if alcohol be present. Ether and alcohol may also be detected by shaking the chloroform

with water in a graduated burette, when the volume of the latter should remain the same if pure.

Some acids may also be present but are not usually found: Hypochlorous acid detected by its bleaching power; Sulphurous acid by its action on starch and iodic acid; Hydrochloric acid by acid reaction and silver nitrate; Methyl compounds are sometimes present, and may usually be detected by shaking the chloroform with strong sulphuric acid, when a brown colour will be produced. The specific gravity should be from 1.49 to 1.50.

SANTONINE AND STRYCHNINE.

Very serious accidents have happened from the accidental administration of strychnine by mistake for santonine. The latter is usually in scales and of a slightly yellow colour, occasionally colourless, the former is sometimes in rhombic crystals, but more usually in powder and perfectly white. Strychnine is easily soluble in dilute acids, santonine is not. Strychnine gives an evanescent purple colour with potassium chromate and sulphuric acid, santonine does not. Strychnine and its salts are intensely bitter, santonine is not.

The writer would advise all druggists to keep poisonous substances in *three cornered bottles*, the peculiar feel of the bottle will at once arrest attention.

ALCOHOL.

The strength of alcohol may be ascertained by taking its specific gravity and referring to the tables appended to almost all works on chemistry. For ascertaining the quantity of pure alcohol contained in wine or beer 4000 grains should be distilled with good cooling apparatus until about 1200 have passed over. The specific gravity of this may then be ascertained either by the specific gravity bottle or other means described at page 100. By reference to tables the amount of alcohol per cent in the 1200 grains can be easily calculated, and from this the per centage in the wine or beer experimented on. Suppose the S G is 0.9638, representing 26 per cent. 26 multiplied by 12 will then give the total quantity of alcohol contained in 4000 grains, and from this the per centage can be calculated.



Many wines are slightly acid to litmus paper, owing to the presence of acid salts, of tartaric or other fixed acid, but if the distillate should also exhibit an acid reaction it will indicate the presence of acetic acid which is volatile. If in any quantity it will show that acetous fermentation had set in and that the wine or beer is more or less spoiled.

ETHER.

Should be perfectly neutral to litmus paper. It often contains alcohol, the amount of which can be roughly estimated by mixing in a graduated burette 50 measures of the ether with 50 measures of water, shaking up, allowing to settle and observing how far the 50 measures of ether have been diminished. The slight solubility of ether in water (1 in 10) must be taken into account.

RE-AGENTS.

The following re-agents have been omitted in their proper place :

POTASSIUM BICHROMATE.

The commercial salt purified by re-crystallisation may be dissolved in ten parts of water, this salt may be used instead of the chromate.

LEAD ACETATE.

Dissolve the commercial salt in 10 parts of water, and filter.

SILVER NITRATE.

The commercial salt should be re-crystallised and dissolved in 20 parts of water.

CALCIUM SULPHATE.

Pure gypsum or precipitated sulphate should be macerated with cold water for some hours and filtered, or it may be boiled with water, allowed to cool and filtered.

POTASSIUM IODIDE.

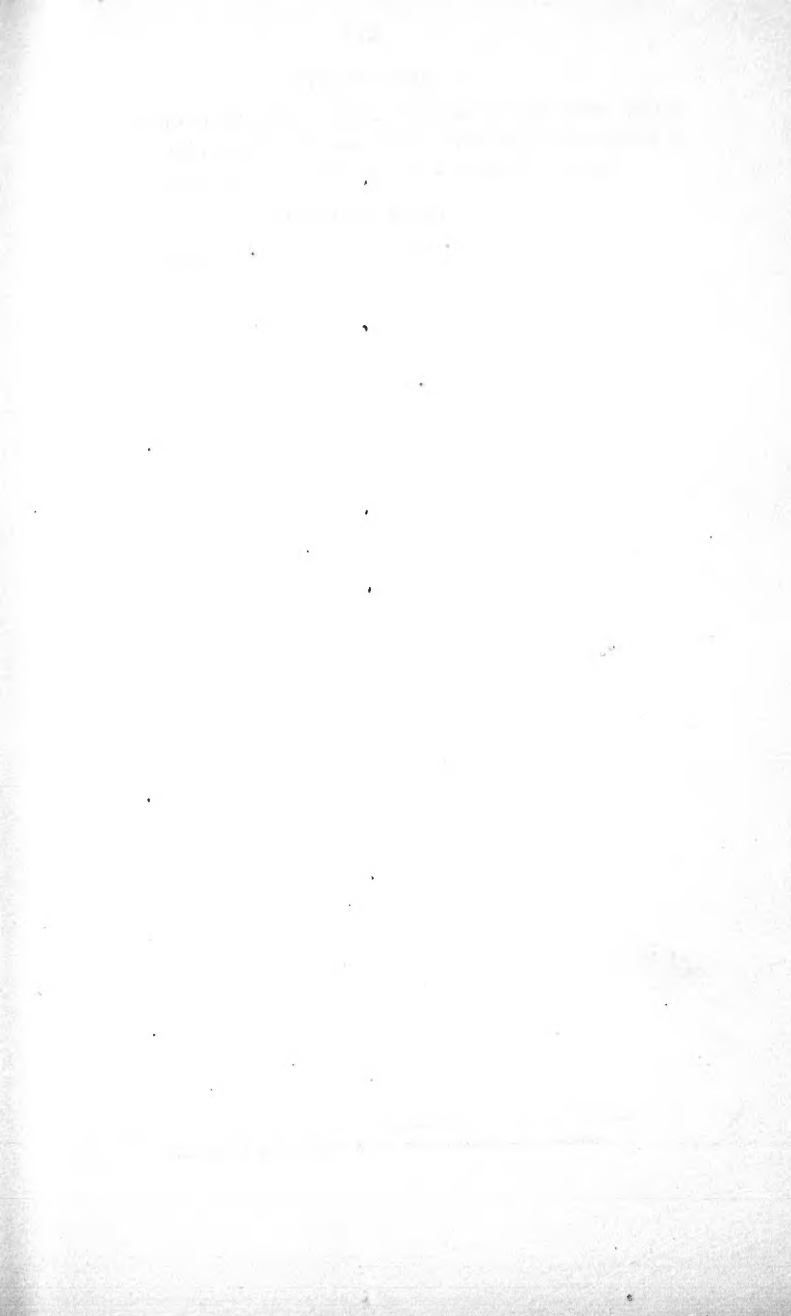
Dissolve in 10 parts of water. The solution should be colourless.

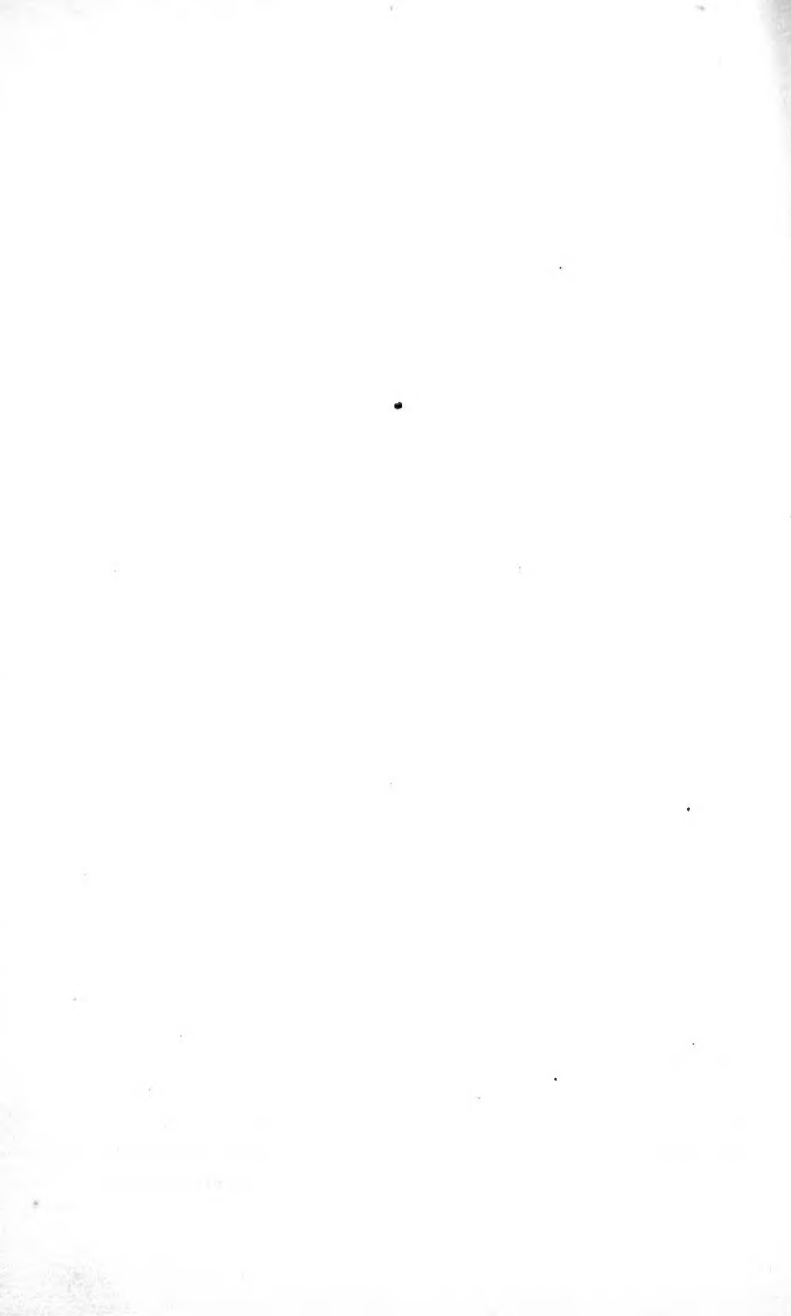
SOLUTION OF INDIGO.

Mix one part of powdered indigo with 5 or 6 parts of sulphuric acid kept cool, allow to stand some hours, dilute with 20 parts of water and filter.

AMMONIUM SULPHIDE.

Hydrosulphuric acid gas is passed into moderately strong ammonia until fully saturated, that is until the liquid ceases to give a precipitate with salts of magnesia. Its true formula is $\text{NH}_4\text{H.S}$ hydrosulphide of ammonium, if mixed with the same quantity of ammonia as first employed it becomes true sulphide $(\text{NH}_4)^2\text{S}$. Either solution may be used. After a time it is apt to become colourless, and is then of no use.





LITMUS PAPER.

A few lumps of this substance may be boiled in one or two ounces of water, the solution filtered, and strips of filtering paper soaked in it. For red paper a very slight trace of acid must be added.

TURMERIC PAPER.

The solution must be made with alcohol.